Lecture MS_1

Mineral Systems Overview

From Barnicoat & Hobbs

Ore deposits are economic accumulations of metals one to three or more orders of magnitude more concentrated than average crustal levels. These accumulations develop either as a result of the transport of ore-forming elements followed by their preferential deposition in a restricted volume, or by the selective dissolution of non-ore-forming elements and their transport away from the site of dissolution. A range of processes control the development of these concentrations, and the geological expression of the processes have been codified into the concept of *Mineral Systems* by Wyborn et al (1994). These authors defined a mineral system as 'all geological factors that control the generation and preservation of mineral deposits', based on the concept of Petroleum Systems formalised by Magoon & Dow (1991). The system perspectives of Wyborn et al (1995) and Magoon & Dow (1991) are both based around a three-fold focus on sources, transport and traps.

The conceptual framework of source-transport-trap is misleading, at least in its simplistic application. No matter what the original composition of a fluid is it will rapidly interact, both physically and chemically, with the rocks it passes through, and components dissolved in the fluid reflect differing parts of the flow path, depending on their concentrations in country rocks and solid/fluid partition coefficients. So the concept of a special source fluid is unhelpful unless the fluid system never sees the rocks it passes through. It is normal that the fluid originates from one source, whilst metals and complexing anions are sourced from several other sources. Thus most "bucket" type (i.e. non reaction-transport) chemical models are likely to yield a result implicit in the starting assumptions. The concept of a trap, paralleling the usage in petroleum systems is also unhelpful as it implies that the fluid flow, and if this is the case, it would be

impossible to transport sufficient material to form an ore body. An anticlinal hinge with a seal on top is exactly the wrong setting for an ore body unless other far more important processes such as breaching of the seal are also operating. Further points not explicitly described by a source - transport - trap framework include tectonic setting, which controls the source term, and the architecture, which controls the transport paths. It has increasingly been recognised that such factors are critical to understanding the siting of ore bodies.

Mineral Systems and the Five Questions

More recently the mineral systems framework has developed to explicitly consider the critical geological features necessary for the development of concentrations of material. An approach known as the 'Five Questions' was developed in the Australian Geodynamics Cooperative Research Centre (AGCRC), and summarised in Walshe et al. (2005). The five questions are:

1. What are the geodynamic and P-T histories of the system?
2. What is the architecture of the system?
3. What are the fluid reservoirs?
4. What are the fluid flow drivers and pathways?
5. What are the metal and sulphur transport and depositional processes?

By answering these question a about a mineral system, the definition of Wyborn et al (1994) is fulfilled and the system and its context can be fully described. The full context is extremely important, as it provides information on the drivers of the processes that lead to the development of mineral deposits. An example of this approach to understanding ore formation is give in Ord et al (2002), who investigated the origins of the Century Zn-Pb orebody in northern Queensland. The five questions make explicit the range of features that should be considered to understand the development of mineralisation, and they reveal the necessity to think across scales from that of the geodynamic setting to the depositional

environment. As much as anything else, this should include considering the *chemical architecture,* covered in the question concerning fluid reservoirs, at scales ranging from depositional sites upwards. Of course, this is not intended to suggest that consideration of the geodynamic setting of mineralisation is new - links between nature of mineral systems and their global setting have been discussed since soon after the time that plate tectonics became established (e.g. Sillitoe, 1972; Spooner & Fyfe, 1973; see also Sawkins, 1984; Russell, 1992) and work continues on this topic (Groves & Bierlein, 2007).

Experience has revealed that using the five questions does ensure that all aspects of the context of a mineral system are considered. But are the questions sufficient to fully evaluate the processes responsible for ore formation? In the next section, the controls on the development of concentrations of ore elements are analysed.

Fundamental controls on ore formation

As noted in the introduction, the concentration of ore elements in a deposit arises either by transporting the appropriate material in to a site or by removing diluents. A simple expression can be written that considers the rate of deposition:

Rate of Deposition = mass flux of transport medium x gradient in carrying capacity

as it is *changes* in the carrying capacity of the transport medium that lead to deposition (Walsh et al., 1984; Rimstidt 1997). As written, this expression neglects diffusion and dispersion. Without a decrease in carrying capacity, all of the element in question will continue to be carried by the fluid. In cases where material removal is the critical process, the deposition rate will be negative. Over time, the quantity of deposited material builds up, with the amount of material deposited given by the integral of the deposition rate with respect to time. For example:

- The rate of heavy mineral deposition is given by the water flow rate multiplied by the change (gradient) in entrainment capacity. Entrainment capacity is proportional to velocity^2 (Bagnold, 1966; Allen; 1997).
- The rate of ore formation in magmatic systems is specified by the rate of magma supply and changes in the solubility of the elements of interest due to changing temperature, composition, etc.
- In hydrothermal systems, the fluid flow rate and changes in solubility due to changes in P, T and chemistry are responsible for deposition.

It is possible to analyse the response of hydrothermal systems in more detail, following an analysis outlined by Phillips (1990; 1991; see also Cathles & Adams, 2005). They show that the rate of deposition of the element of interest, Q, is given by:

$$Q = -v\nabla c_e = -v \bullet \left(\frac{\partial c_e}{\partial T} \nabla T + \frac{\partial c_e}{\partial P} \nabla P + \Sigma_r \frac{\partial c_e}{\partial c_r} \nabla c_r \right) \qquad (1)$$

where

v is the fluid flow velocity in kg s^{-1},

c_e is the equilibrium concentration in the fluid of the element of interest in mol m^{-3},

T is the temperature in K,

P the pressure in Pa and

c_r the concentration of other elements (species) that influence c_e in mol m^{-3}.

∇ is the gradient operator such that $\nabla T = \partial T/\partial x + \partial T/\partial y + \partial T/\partial z$, and the

• between the fluid flow velocity and the bracketed terms signifies the scalar
  product of vector quantities, the velocity and the gradients.

This is critical as the rate of deposition is maximised when the flow is perpendicular to the gradient(s). Equation (1) is merely the mathematical expression of the relationship noted at the beginning of this section, and states that deposition rate is given by the fluid flow rate and sum of the products of solubility sensitivities with respect to T, P and the concentration of other species multiplied by the spatial gradients in P, T and concentration respectively. The minus sign is required as the rate of solid production is the opposite of the

change in fluid composition yielded by the solubility sensitivity terms. As above, the equation omits a dispersion/diffusion term (c.f. Phillips, 1990; 1991) as such effects are negligible over distances that P and T vary. Precise application of the principles discussed here would require inclusion of such terms, but their omission does not impact upon the analysis presented here. Equation (1) has been used by Hanor (1994) and Hobbs & Ord (1997) to explore process in sedimentary basins and mineral systems respectively.

A key assumption in using equation (1) is that local equilibrium is maintained. Given that reactions take some time, flow of fluid could lead to significant transport before equilibrium is attained. The equilibration length, l, due to advection can be estimated using the following equation (Phillips, 1991; Zhao et al., 2006):

$$l = \frac{v}{\Phi k_r} \qquad (2)$$

where

v is the Darcy fluid fluid velocity,

ϕ the porosity and

k_r the overall chemical reaction rate (s^{-1}).

Flow velocities may be of the order of 3 x 10^{-8} m s^{-1} (1 m yr^{-1}) in meteoric water flow regimes (e.g. Harrison & Summa, 1991), and compaction-driven flow rates are typically about 15% of the meteoric value (i.e. 3 x 10^{-9} m s^{-1}; 10 cm yr^{-1}).The focussing of fluid flow into more permeable zones means that values there will typically be say 15 times greater – 4.5 x 10^{-8} – 4.5 x 10^{-7} m s^{-1} (Zhao et al; 2006). The migration of seismicity in the Mammoth Mountain area of the Long Valley caldera has been interpreted to result from the propagation of fluid-filled cracks by Hill & Prejean (2005). Seismicity front migration rates of up to 2 km/month (~8 x 10^{-4} m s^{-1}), considerably more rapid than estimates of fluid flow caused by other processes. Overall reaction rates may be estimated from experimental studies as the rate is given by the reciprocal of the time take to reach equilibrium compositions. Table 2 lists some values drawn from a variety of literature sources. From this it can bee seen that reaction rates at 300°C typically range

from 6 x 10^{-6} to 8 x 10^{-8} s^{-1} with a wider range at lower temperatures. Using equation (2), equilibration lengths can be calculated. At the highest flow rates, equilibration distances stretch beyond kilometre scale, otherwise they are less than that. The assumption of local equilibrium is thus quite adequate to be useful in identifying critical parameters controlling ore deposition.

The fluid flow velocity, used in equation (1) can be derived from Darcy's Law, which describes fluid flow in porous media:

$$u = \frac{k\rho g}{\mu} \cdot \nabla H \qquad (3)$$

where

u is the *Darcy flow velocity,* related to the true fluid flow velocity by $v=u/\phi,$

k is the permeability of the medium,

ρ the fluid density,

g the acceleration due to gravity,

μ the fluid's viscosity and

H the hydraulic potential (strictly, H is the hydraulic potential plus terms describing the effect of changing fluid density with pressure and temperature, but for our purposes the simplification is adequate). In addition, equation (1) can be integrated with respect to time to yield an expression for the total amount of material deposited, A:

$$A = \int - \Phi \frac{\kappa \rho g}{\mu} \nabla H \cdot \left(\frac{\partial c_e}{\partial T} \nabla T + \frac{\partial c_e}{\partial P} \nabla P + \sum_r \frac{\partial c_e}{\partial c_r} \nabla c_r \right) dt \qquad (4)$$

where t is time.

Equation (4) reveals that there is a suite of factors that control the amount of material deposited. Several of these are intrinsic features of the system and the fluid involved – fluid density and viscosity, and the acceleration due to gravity. Other factors are controlled by the nature of the system itself, and hence are independent controls on the amount of material (ore) formed:

1. Permeability
2. Gradient in hydraulic potential

3. Solubility sensitivity of the element of interest with respect to *P, T* and c_r

4. Spatial gradients of *P, T* and c_r
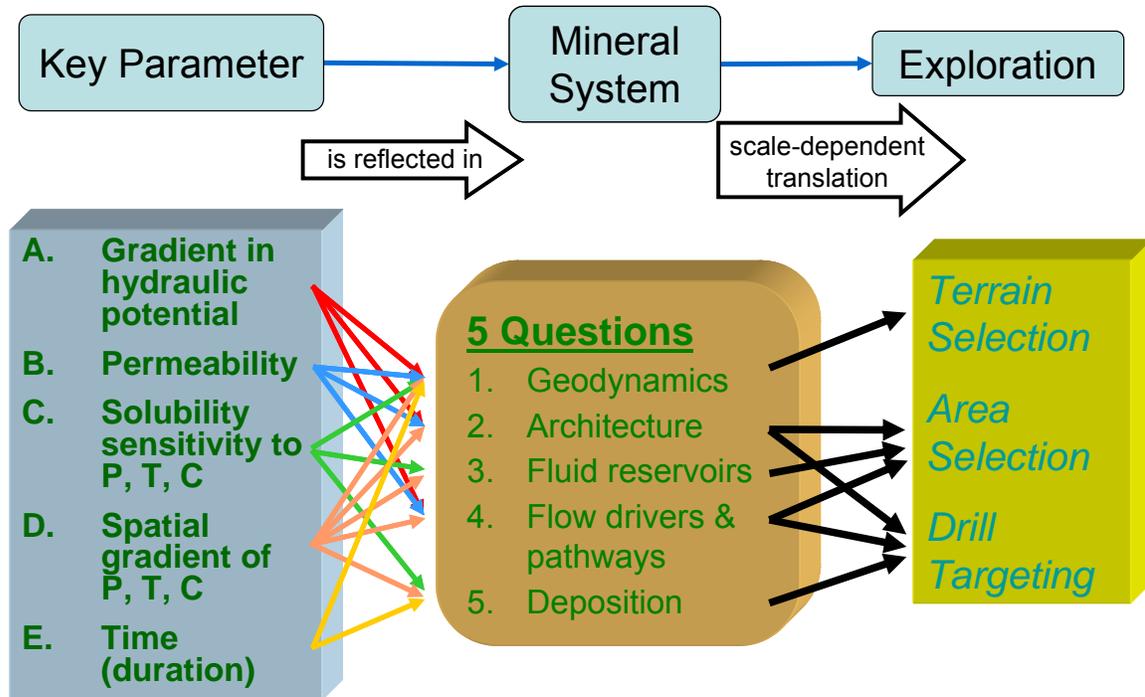
5. Time (duration of the system)

Figure 1. Linkages within a Mineral Systems framework between the key parameters and (derived from the basic relationship in the text), the Five Questions and exploration..

Permeability

Permeability varies hugely in geological systems, with values in nature (summarised recently by Rowland & Sibson, 2004) spanning more than 10 orders of magnitude from<10^{-21} m² in shales, fault zone core gouges and unfractured igneous and metamorphic rocks to >10^{-10} m² in karst limestones and near-surface, permeable basalts. Permeability in rock masses is related to two characteristics of the material – the interconnectedness of pores between the particles/grains/crystals and to open fractures. The permeability, k due to interconnected porosity, ϕ, in materials is frequently modelled using the Kozeny-Carmen relationship ($k \propto \phi^3$; see Ingerbritsen & Sanford, 1998), though Mavko &

Nur (1997; see also Cox et al.2001) notes that this relationship is only reasonable at porosities somewhat larger than the percolation threshold values at which an interconnected network of pores develops. The permeability of arrays of parallel fractures can be estimated using the relationship:

$$\kappa_f = \frac{Na^3}{12} = \frac{a^3}{12d}$$

where k_f is the fracture permeability, N the number of fractures per unit length, a the fracture aperture and d the fractures spacing (e.g. Cox et al; 2001). Values calculated using this expression range from 8 x 10^{-20} m^2 for 1μm fracture every 1m to 8 x 10^{-16} m^2 for a 10μm fracture every 10 cm and 8 x 10^{-9} m^2 for a 1mm fracture every 1cm. Cox (2005) discusses more sophisticated formulations for randomly oriented fractures that are not fully connected. The propagation of microseismicity allows estimates of bulk-rock permeability, and values of 10^{-18}-10^{-14-} m^2 have been derived using such data (e.g. Shapiro et al., 1999; Rowland & Sibson, 2004; Hill & Prejean, 2005). , Permeabilities >10^{-16} are typically considered necessary to allow convection to occur. This is reasonably appropriate for large systems with a vertical extent of the order of 10 km if viscosities, heat capacities and thermal expansions at deeper, hotter levels in the system are assumed. Permeabilities higher than this are needed for systems of smaller (and more realistic) vertical extent and also systems at lower temperatures. A further complexity is introduced if phase separation occurs (Geiger et al, 2005).

Permeability is mineral systems is often viewed as being created by faults and fractures, as such structures host many (most?) ore deposits. Critically, however, ore bodies are most frequently located on structures smaller than the dominant features in an area. A variety of explanations have been advanced for this observation… It is also recognised that rocks, in particular coarse-grained sediments can act as zones of enhanced fluid flow. Such domains are often considered as providing the fluids for fault/fracture systems that allow focussed flow needed for ore formation. The distributions of appropriate sedimentary

facies, together with the patterns of diagenesis are thus important controls on permeability distributions.

Gradients in hydraulic potential

Gradients in hydraulic potential are the drivers for fluid flow. The hydraulic potential at any point is the difference between the actual fluid pressure and the hydrostatic pressure under the same P-T conditions. Hydraulic potential gradients may be created by factors such as topography, devolatilisation, crystallisation of magmas, buoyancy and deformation. Topography generates gradients in hydraulic potential because elevated areas of recharge (of necessity sub-aerial) are hydraulically connected to lower-lying discharge sites. Devolatilisation, leading to localised increases in fluid pressure, may be driven by metamorphism but also includes fluid release during diagenesis and the production of petroleum. The significance of petroleum formation is often underestimated in basinal systems, where is may be very important in driving the flow of aqueous fluids (Eisenlohr et al., 1994; Cathles & Adams, 2005). Both felsic and mafic magmas may release fluids on cooling and crystallisation; the composition of the liberated fluids varies with both magma chemistry and pressure. Buoyancy effects often lead to hydraulic potential gradients that drive fluid flow. They may be derived from either temperature or compositional variations causing spatial variations in fluid density. Deformation can cause dilation linked to faulting and fracturing (Sibson, 1987, 2001; Cox, 2005). Deformation may also be due to compaction in sedimentary sequences and by the closure of porosity due to inelastic deformation or reactions. Theses changes in porosity affect fluid pressure and hence fluid pressure gradients.

Solubility sensitivities

Solubility sensitivities can be derived from measured or calculated solubilities; figure 1 illustrates this for SiO_2 solubility derived from quartz. When $\partial c_e/\partial T$ is positive, solubility increase with temperature and conversely, deposition is caused by decreasing temperature. Similarly, when $\partial c_e/\partial P$ is positive, solubility increases with increasing pressure and pressure reduction leads to deposition.

As shown in figures 1 and 2, solubility sensitivity is typically positive with respect to temperature and hence cooling will frequently lead to deposition. There are some well-known instances of retrograde solubility where $\partial c_e/\partial T$ is negative: minerals displaying retrograde solubility include calcite and anhydrite (e.g. Rimstidt, 1997). The dependence of solubility on pressure is more complex, and sulphides often show negative values of $\partial c_e/\partial P$ over specific ranges of PT conditions. This is illustrated in figure 2 which illustrated calculated sphalerite solubility. At low pressures and high temperatures, for the conditions modelled, $\partial Zn/\partial P$ is negative and hence a decrease in pressure leads to dissolution of sphalerite. Comparison with figure 1 shows that quartz does not show such behaviour, so pressure reduction at high temperatures, such as could occur during the opening of vein systems, could lead to sphalerite resorption and quartz deposition (figure 3). Such effects have been discussed previously by Helgeson & Lichtner (1997). Pressure change will have an especially significant effect on solubility when it leads to phase separation. Figure 4 shows how the solubility of gold in CO_2-bearing dilute NaCl solutions changes significantly when a fluid phase separates.

In undersaturated solutions, $\partial c_e/\partial T$, $\partial c_e/\partial p$ and $\partial c_e/\partial c_r$ will be zero. Changes in P, T and composition can cause the sensitivities to become non-zero. Changes in fluid chemistry, can be induced either by changes in the mineralogy of rock in equilibrium with the fluid (in other words by fluid-rock reaction) or by fluid mixing. Mixing of fluid with differing chemistry as well as with fluids of different temperature and cause deposition with deposition possible if the second derivatives $\partial^2 c_e/\partial c_r^2$ or $\partial^2 c_e/\partial T^2$ are positive (figure 5).

Solubility sensitivities vary with physical and chemical conditions. They are generally higher at higher temperatures as solubilities themselves are elevated but undersaturation, anticipated to be more prevalent with increasing T, can reduce values to zero. Magmatism is an obvious factor that can significantly affect solubility sensitivities by producing high-temperature fluids at or close to saturation. Metamorphic grade, correlating as it does with temperature, may also help to demonstrate conditions when $\partial c_e/\partial T$ values are appropriate.

Spatial gradients in P, T and c_r

Spatial variations in P, T and fluid chemistry are ubiquitous within the earth. Many, however, are small and hence lead to extremely gradual changes in solubility and inconsequential (from the perspective of ore formation) changes in the quantity of a mineral. Localised, rapid variations in conditions are necessary to give suitably large spatial gradients in P, T and fluid chemistry for ore formation to occur.

Pressure gradients will (transiently) be greatest around dilational sites associated with structures, in particular features such as dilational jogs. Fluid inclusion data has been used to document transient changes in fluid pressure in fault systems (*amplify*) that reflect the temporary establishment of pressure gradients around structurally-induced fluid flow paths. Such situations will act not only to maximise the solubility gradients (the products of solubility sensitivity and spatial gradient) – see equation (1)) but also to increase the gradient in hydraulic potential. Such sites also mark the location of enhanced permeability, hence their widely recognised significance as loci of ore formation. However, smaller gradients at low pressures are also potentially significant as they can lead to lead to high solubility gradients as solubility sensitivity can peak at low pressures due to phase separation (figure 4).

Temperature gradients are greatest near the surface, and around magmatic centres. *Chemical gradients* may be due to (a) fluid-rock disequilibrium, which will be affected by both temperature and compositional effects, and be maximised at the transition from one lithology to another, or (b) fluid mixing. Fluid mixing will only be effective if it results in gradients in c_r when $\partial^2 c_e / \partial\, c_r^2$ is positive (c.f. figure 5). Concave up solubility curves, which possess positive values of $\partial^2 c_e / \partial\, c_r^2$, are characteristic of situations where ratio of the element of interest to the complexing

element is greater than 1. For example, $\partial^2 Zn / \partial\, Cl^2$ is positive for complexes with more chlorine than $ZnCl^+$.   Under these circumstances, mixing leads to the development of over saturation a and hence deposition.

Time

Steep gradients in P, T and c_r are normally transient in nature. However, there are situations when gradients may be maintained for significant durations or may develop repeatedly. Such situations include:

- Near the earth's surface, where temperature and compositional (especially redox) gradients will be elevated for long periods.
- Areas subject to repeated igneous activity, where temperature gradients may remain high, and where high pressure and compositional gradients may be repeatedly developed.
- At sites where hydraulic seals repeatedly develop and breach.
- At locations that undergo repeated deformation-induced dilation effects.
- Where a stable hydrology develops.

Several of these factors will also lead to longevity of other favourable conditions: magmatism has occurred as a favourable factor as a source of hydraulic potential, and solubility sensitivity, and sites of dilation which also have elevated hydraulic gradients and permeabilities

Some of these parameters translate readily to mappable features that have concerned exploration geologists for many years. Permeability is related to the distribution of structures and of permeable sedimentary facies, for example. A preliminary look at the parameters and what controls them yields the following three sets of geological inputs:

- **Palaeogeography:** feeds into most of the critical factors
    - Describes distribution of (emergent) topography and hydrocarbon generation potential, both potential sources of hydraulic gradient.
    - Controls distribution of facies and diagenesis that control permeability distribution in sedimentary sequences.
    - Describes potential source regions for meteoric fluids (emergence again) and brines in marginal marine areas: key control on solubility sensitivity.

- o Allows identification of stable areas where P & t gradients could have been stable for long periods.

- **Magmatism:** also plays a major role in many critical factors

  - o Source of fluids and temperature distributions that may create hydraulic gradients.

  - o Driver for fracture generation and hence a control on permeability.

  - o Creates spatial gradients in temperature (and potentially chemistry too).

  - o Act as a fluid source the nature of which will depend on the magma's origin: key control on solubility sensitivity.

  - o Repetitive magmatism will lead to long-lived hydrothermal systems.

- *(Structural) Architecture*

  - o Controls the distribution of dilation sites that play an important role in developing hydraulic gradients.

  - o Defines most of the high-permeability domains in the crust

  - o Helps to define pressure gradients, and plays a role in facilitating fluid mixing.

  - o Repeated failure on structures (including reactivation of deeper features) allows prolonged fluid movement an/or multiple deposition/mixing/etc. events.

Barnicoat, A. C. (2008). The Mineral Systems approach of the pmd*CRC. New Perspectives: The foundations and future of Australian exploration. Abstracts for the June 2008 pmd*CRC Conference., Perth, Geoscience Australia Record 2008/09.

Bruce Hobbs: CAN ONE BE PREDICTIVE IN MINERAL EXPLORATION?