# Chapter 1. INTRODUCTION.

**September_9_2016.**

## 1. Introduction.

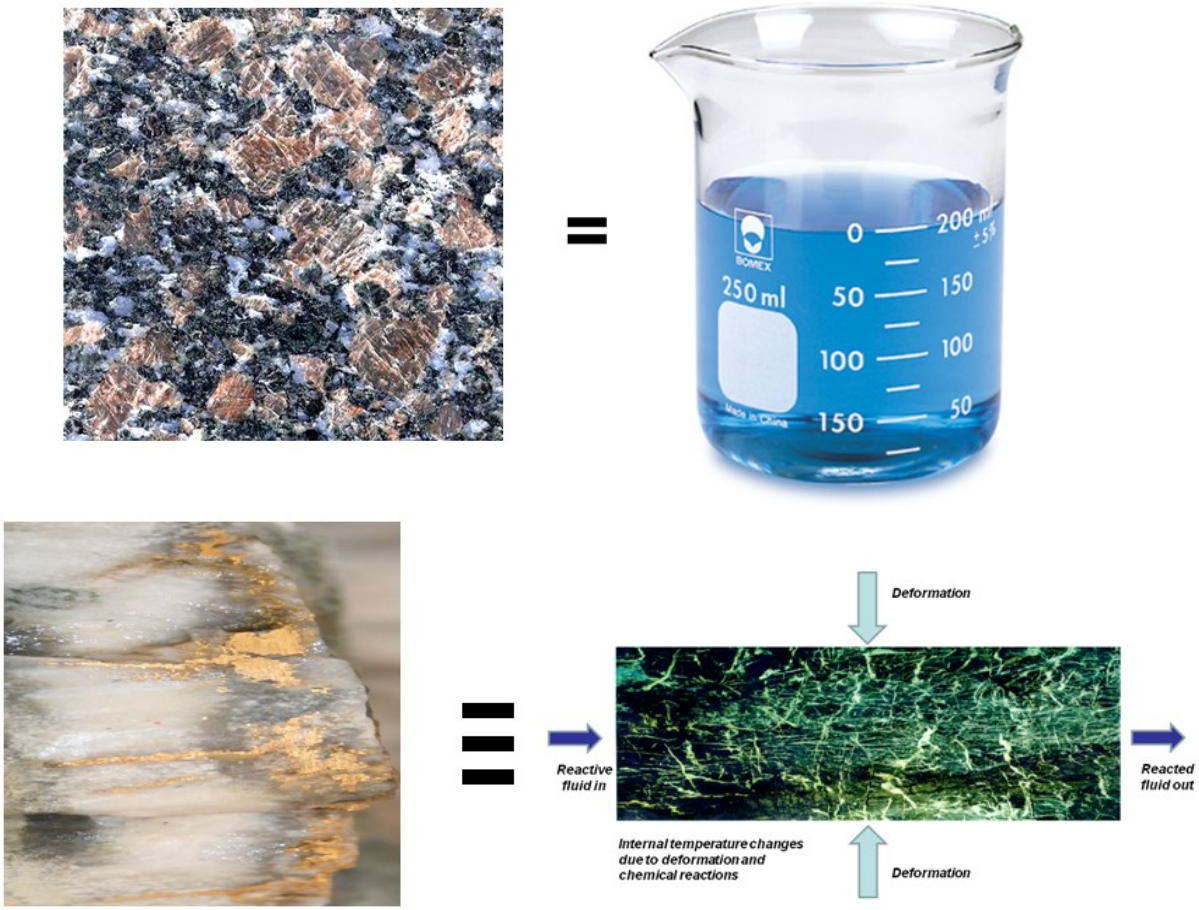
The formation of hydrothermal systems and their associated patterns of rock alteration, veining, brecciation and mineralisation present one of the most scientifically challenging parts of the geosciences. These systems are examples of the ultimate in full coupling between mechanical, hydrological, thermal and chemical processes and operate as highly nonlinear entities. An understanding of the processes involved in the formation of these systems is of fundamental economic importance in a world that has a continuing demand for metals in a scientific and industrial environment where discovery rates are declining and the cost of discovery is increasing. For over 100 years scientific investigations of hydrothermal systems have been directed at studies of individual mineral deposits at ever increasing detail but still with no unified view of what controls the location, size and grade of individual deposits. Perhaps more recently the discipline has adopted more of a systems approach where the mineral deposit is viewed as part of an integrated crustal or lithospheric scale system in which a number of processes associated with fluid production, transport and mixing and metal deposition are considered together. Still the fundamental principles and parameters that define location, size and grade have not emerged in any coherent manner. For the most part, the traditional view of mineralising systems has been grounded in concepts associated with linear system behaviour, a view that is embedded in the source-transport-trap concept of mineral systems. The outstanding example of linear system behaviour is an assumption that chemical equilibrium thermodynamics controls what we see.

This book is meant to be an introduction to an integrated framework that examines the various processes involved in the formation of hydrothermal systems within the lithosphere of the Earth and attempts to enunciate the critical parameters that define why a particular system is where it is and not some-place else, why the alteration system looks like it does, why the system is high grade, disseminated, vein, breccia or stock-work hosted, why the system is small or large, why the grade is high or low and why the grade has the spatial patterning and distribution that is observed. Such a framework must also define measurable data sets that can be queried in some manner that is useful to the mineral explorationist and that enables her or him to discover, more efficiently, new deposits in the future.

The essence of our approach is that hydrothermal systems remain far from equilibrium throughout their development. Many people would respond by basically agreeing with such a proposal but are then constrained by the lack of any formalism that enables one to make any further progress. The ultimate response commonly is that even if these systems are never strictly at equilibrium the processes are so slow that the system is so close to equilibrium that equilibrium, or at least "local equilibrium" can be assumed and so the suite of thermodynamic tools that has been developed since Gibbs (and especially in the classical *solution chemistry* studies of workers such as Garrels and Helgeson) can be applied with considerable confidence. As Lindgren pointed out 90 years ago:

*"The fact seems to be that physical chemists are so used to consider systems in equilibrium and reactions in open space or in liquids that they give little attention to other conditions."*
W. Lindgren (1925, p.25)

The point is made in the Figure below where we contrast the traditional, equilibrium Garrels –Helgeson aqueous geochemistry approach with that of a view of mineralising systems as non-equilibrium, open flow deforming chemical reactor.




Our response to the local equilibrium view is that these systems really are never close to equilibrium and that there is a very well developed formalism that enables such systems to be described, modelled and understood in terms of non-equilibrium thermodynamics; chemically this formalism is similar but not identical to that developed for metasomatic systems by Korzhinskii (1950) and has been summarised by Ross (2008). A system at equilibrium is dead; there are no processes operating. By definition one can never understand the processes that operate in a system if one adopts a formalism based on equilibrium since the final equilibrium state is independent of the path followed to reach equilibrium. Our contention is that hydrothermal systems, whilst they are forming, are living, vibrant, evolving entities that are forced to pass through a number of well-defined and constrained modes of operation for as long as fluids and heat are supplied to the system and whilst the relevant mineral reactants are still present. These processes and operational modes leave their marks in the rocks and the messages are there for all who know how to read them. The messages are written using the grammar of nonlinear dynamics and of non-equilibrium physical and chemical

thermodynamics, not of chemical equilibrium thermodynamics. As such this book forms an introduction to the non-equilibrium thermodynamics of hydrothermal systems.

Even so, this book is intended to be a straightforward, non-technical consideration of the characteristics and evolution of hydrothermal mineralising systems with the overall goals of:

- Discussing the processes and mechanisms, from the atomic to lithospheric scales, whereby hydrothermal mineralising systems are formed;
- Understanding and quantifying the irregularity and unpredictable nature of mineralising systems and relating such understanding to the processes and mechanisms that formed the systems; and
- Developing a new paradigm for hydrothermal mineralising systems to aid in the discovery of new mineral systems.

The subject matter considered here is frequently clouded with mathematical and chemical arguments that are difficult for many geoscientists to grapple with. Our intent is to present the material with a minimal emphasis on the mathematical and chemical aspects of the problem. We give an annotated reference list at the end of each chapter for those interested in further technical development of the subject matter. This introductory chapter is meant as a summary of the whole book so that the reader can see where we are going to. We discuss the three dot points above in this chapter.

The messages from this book are:

**1.** ***Evolving systems***. Hydrothermal systems are living, evolving, vibrant things, not dead objects at equilibrium. The modes of operation and evolution of the system can be read in the rocks but one needs the right language to read these stories.

**2.** ***Nonlinear dynamics.*** The evolution of these systems is nonlinear so do not interpret what you see in a linear manner. The last 50 years of developments in nonlinear dynamics are available to read the messages left in the rocks. The whole tool box of "chaos theory" is available. In particular, large hydrothermal systems are *critical* systems, where the word *critical* has a much wider meaning than is used in the concept of self-organised criticality, and so the last 100 years of developments in concepts and analytical tools are available also.

**3.** ***New analysis tools.*** One would not use statistics to interpret magnetic or gravity data; one uses the physics behind the process, namely, potential field theory. So why do people use statistics to interpret ore grade or to attempt correlations between structural and chemical data sets? We propose that one uses techniques based on the physics and chemistry of the processes involved instead of empirical statistics based approaches.

Above all, we search for surrogates for mineralising processes that can be quantified by field and/or laboratory measurements/observations. The Holy Grail comprises some quantities that scale differently for "failed" or for small deposits as opposed to "successful" or large deposits.

### 1.1. The processes and mechanisms whereby hydrothermal mineralising systems are formed.

In this book hydrothermal systems are viewed as giant chemical reaction vessels that are held far from equilibrium by the influx of heat and of fluids that contain economically important

metals in solution. In addition, these systems are commonly also under the influence of lithospheric scale deforming motions that also add to the non-equilibrium nature of the system. The essential problem to be addressed is: *What are the characteristics of non-equilibrium systems that result in the formation of economically viable deposits of metals and how can we recognise these characteristics in ways that are more efficient and effective than in the past?* The answer to this question is encapsulated in the following statement: ***The evolution of successful systems results from competitive processes.***

Systems not at equilibrium are always under the influence of competitive processes. The systems are forced from equilibrium by processes that do work on the system and hence provide energy to the system. The processes that interest us are those that result in *gradients* in deformation, temperature, hydraulic head, or chemical potentials. On the other hand, the systems tend to evolve towards equilibrium through processes that dissipate energy. Those dissipative processes that correspond to the above gradients are: diffusion of stress generally stated as diffusion of momentum, heat flow, fluid flow, and transport of chemical species. By dissipation we mean the conversion of work done by mechanical, hydraulic and chemical processes to heat.

The basic, fundamental principle that governs the formation of mineralised hydrothermal system involves the competition between a number of processes. Some processes tend to grow the system, others tend to shut it down. Bejan and Lorente (2010) describe what they call a Constructal Law: *For a finite-size flow system to persist in time (to live) it must evolve such that it provides greater and greater access to the currents that flow through it.* This generally means that competitive processes operate to keep the system alive. A lack of competition leads to death (equilibrium which corresponds to maximum entropy or maximum disorder). Dominance of "growing" processes leads to explosive death. Dominance of "killing" processes leads to slow death. Successful systems are those that are finely tuned between "growing" and "killing" processes. So, with these principles in mind let us look at the evolution of hydrothermal systems held far from equilibrium by inputs of heat and fluids that bear reactive chemical species.

Hydrothermal mineralising systems are multi-scale in the sense that processes responsible for the evolution of these systems operate at all spatial scales from the molecular to the lithospheric (Figure 1.1 a). At each of these scales one can adopt a non-equilibrium thermodynamic approach where, at that particular scale, a set of energy producing processes competes with dissipative processes. In addition the processes that operate are spread over at least 30 orders of magnitude as far as time scales are involved (Figure 1.1 b). This leads to a cascade of behaviours across the spatial and temporal scales that we will consider in greater detail in Section 1.2. The important point that arises from a multi-scale approach is that processes that operate at one scale influence processes that operate at other scales and so the scales cannot always be treated independently of each other. Ultimately one has to develop a homogenisation approach where processes that operate at a scale smaller than of interest are "bulked" or "averaged" in some way so that the details vanish at that smaller scale and some set of mathematical relations are derived to describe the average of the small scale behaviour. These mathematical relations are then used as an input to describing behaviour at the next

scale up. In general all the processes that operate are coupled in a first order manner so that each has a feedback relation on all others. Thus the mechanical-thermal-chemical-hydraulic processes that operate in hydrothermal systems are fully coupled (Figure 1.2) which invariably means that these are nonlinear dynamical systems that exhibit all the chaotic and multifractal behaviours that other coupled systems such as the Earth's climate exhibit.

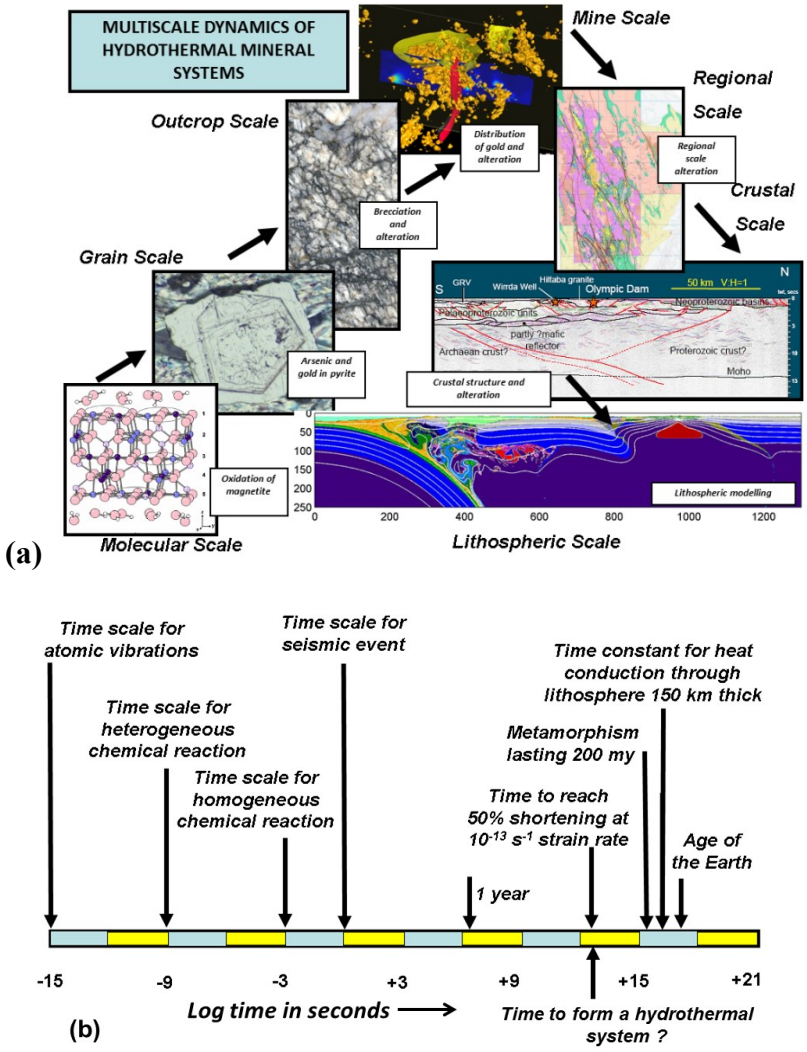



Figure 1.1. The multiscale nature of mineralising systems.

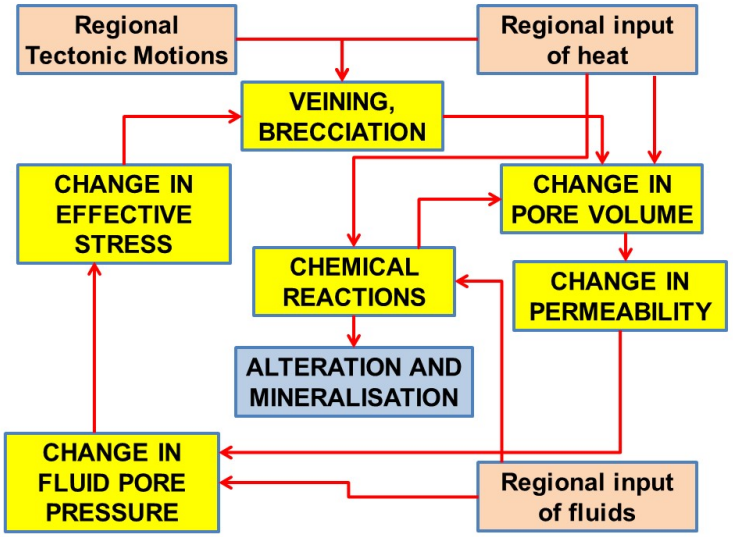



Figure 1.2. Some of the many feedback processes operating in mineralising systems.

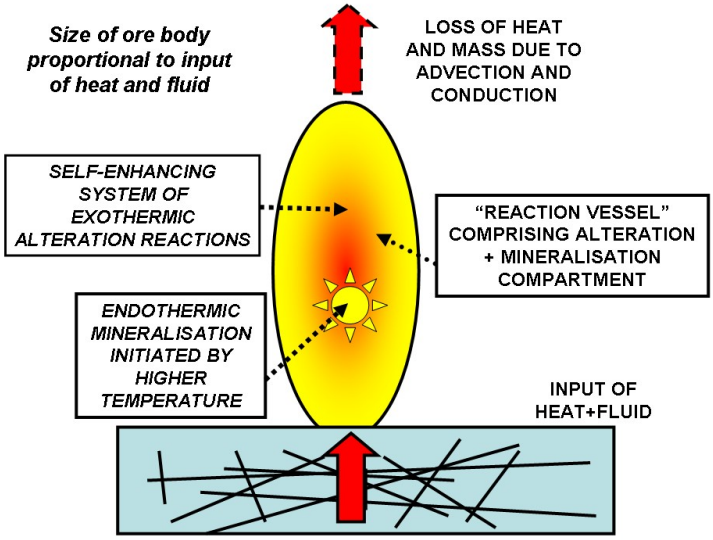



Figure 1.3. One of the end member types of hydrothermal systems: A flow controlled mineralising system.

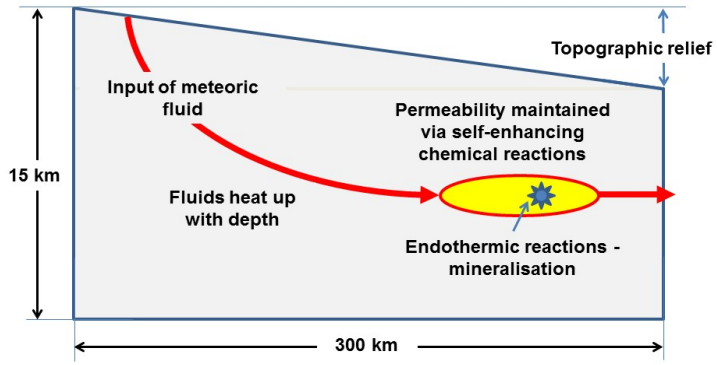



Figure 1.4. A second end member type of hydrothermal system. A hydraulic head controlled system.

In this book we look at hydrothermal systems as nonlinear dynamical systems at all scales from the lithospheric to the grain scales. To us this is a truly holistic systems approach to mineralisation. We emphasise that the "systems" approach that talks about "Source-transport-trap" concepts inherited from the hydrocarbon literature is irrelevant and that hydrothermal

systems are open-flow systems where most certainly no "trap" (in the sense of an impermeable barrier) exists. A "trap" is essential for hydrocarbon accumulation but such a trap inhibits or prevents the development of mineralisation. The system must remain open to the supply of fluids, heat and nutrients and continuity of mass requires that as much fluid leaves the system as enters it subject to the condition that some of the fluid may be consumed or some extra fluid may be generated by chemical reactions within the reactor.

We discuss the evolution of hydrothermal systems as open flow chemical reactors (Figures 1.3, 1.4 and 1.5) in which heat and metal bearing fluids are added to the system and cooler, depleted fluids leave having reacted with the rock mass to produce alteration and mineralisation.

One can recognise four types of thermodynamic systems (Niven, 2009, Niven and Andresen, 2010):

**(a) Isolated systems.** The first is an *isolated* system where extensive variables such as the internal energy density, the volume, and the number of moles of various chemical components are kept constant. The system is isolated from other systems and from its environment by an impermeable wall (Figure 1.5 a). This is also called a *closed system*. The only evolutionary path such systems can adopt is to evolve to equilibrium and the equilibrium state is described by minimising an energy function such as the Helmholtz energy or by maximising an entropy function. If the system is perturbed from equilibrium or begins far from equilibrium the path to equilibrium may be tracked using geometrical methods developed by Gibbs (1906). The path from one state to an equilibrium state may not necessarily be steady. We will see in Chapter 8 that in an isolated system even a simple exothermic reaction of the type $A \rightarrow B$ can produce oscillations in the concentration of A and in the temperature (Gray and Scott, 1994) as the system proceeds to equilibrium. Nevertheless, an isolated system must ultimately proceed smoothly to equilibrium. The behaviour of such a system is that of a closed alteration system (if it could exist) where pseudomorphic replacement (constant volume) mineral reactions are taking place.

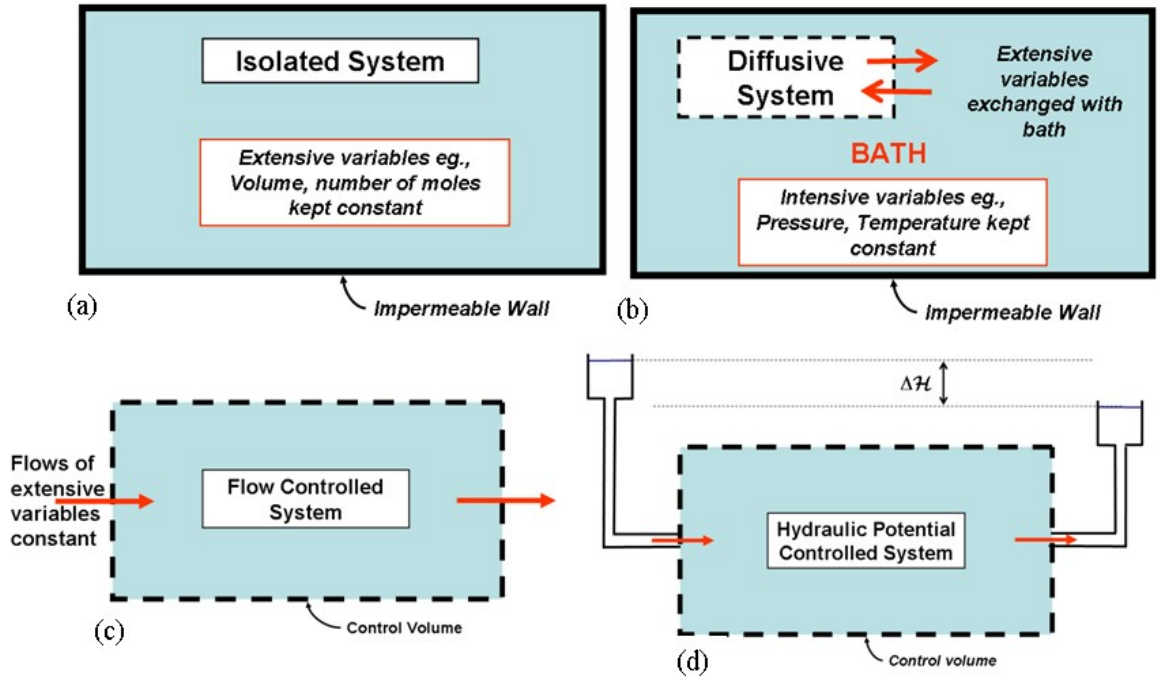



**Figure 1.5.** The four types of thermodynamic systems. (a) Isolated system. Extensive variables are kept constant. The system is isolated from any other system. (b) Diffusive system. The system can communicate with the surrounding bath where intensive variables are kept constant. The bath is isolated from any other system. (c) Flow-controlled system where flows of extensive variables are kept constant within a region known as the control volume. (d) Hydraulic potential, $\mathcal{H}$, control system where the flows of extensive variables are controlled by a gradient in hydraulic potential such as a large mountain range. Both (c) and (d) can communicate with other systems but the evolution of (c) and (d) is controlled only by flows into and out of the control volume and processes that operate within the control volume. From Ord et al. (2012) motivated by Niven (2009).

**(b) Diffusive systems.** The second type of system, a *diffusive* system (Figure 1.5 b) is also a closed system. The system is embedded in another medium which acts as a *bath* and which itself is isolated from all other systems and its environment by an impermeable wall. Intensive variables such as temperature and pressure are held constant in the bath and the diffusive system can interact with the bath by interchange of mass and heat with the bath. Diffusive systems must always evolve to equilibrium and follow the same rules for doing so as do isolated systems except that now the Gibbs energy is minimised at equilibrium.

Clearly most considerations of metamorphic mineral reactions assume the system is isolated or diffusive although the distinction is not commonly well defined or emphasized. In fact, because many metamorphic petrologists regard metamorphic systems as constant mass (as opposed to constant volume) systems they are proposing that metamorphic systems are closed and diffusive. A completely different class of behaviour is that of an *open flow* system (Figures 1.5 c, d) where the system comprises an open configuration that can communicate with the surrounding environment with constraints on mass and heat flow.

**(c) Flow controlled systems**. One of these systems, the third type of system, is an open *flow controlled* system (figure 1.5 c) and is the type of relevance to devolatilising and melting systems and to hydrothermal mineralising systems where the fluid input rate is constrained by the rate of production of the fluid (Phillips, 1991). This we propose also is the case for

orogenic gold deposits and IOCG deposits. The boundaries of the control volume may be fixed spatially or migrate with time. It is important to note that if the flow rate is held constant, the initial porosity and permeability of the system, in general, needs to adjust to new values by mechanical and/or chemical means to accommodate the flow as the system evolves (Chapter 3). The system is characterised by flows of mass and heat through the system and the simplest of such systems is where these flows remain constant in time. These systems evolve to one or more non-equilibrium stationary states[1] and can be held far from equilibrium for so long as the flows are maintained.

**(d) Hydraulic potential controlled systems.** The fourth type of system, a *hydraulic potential controlled flow system* (figure 1.5 d) is similar to a flow controlled system except that the volumetric flow rate is imposed by a gradient in the hydraulic potential such as would be developed by the presence of a large mountain range. These systems evolve in a similar manner to flow controlled systems except that if the hydraulic head is kept constant, the fluid velocity within the control volume changes as the permeability within the system changes due to chemical precipitation and/or dissolution (Merino and Canals, 2012). The thermodynamics of such permeability evolution is considered by Coussy (1995) and by Merino and Canals (2012). In order to achieve a stationary state the rates of chemical precipitation and/or dissolution must evolve. These kinds of systems are typical of MVT and Irish lead/zinc deposits as well as uranium unconformity deposits (Garven, 1985; Garven and Freeze, 1984a, b; Anderson and Garven, 1987; Raffensperger and Garven, 1995a, b: Appold and Garven, 2000; Appold et al., 2007; Murphy et al., 2008). Such systems are also characteristic of many upper crustal shear zones where retrograde metamorphic reactions take place involving the influx of meteoric $H_2O$ (Cartwright et al., 1997).

Some examples of open flow systems are given in Figure 1.6. Open flow systems differ from the classical closed or isolated models used to describe metamorphic and most metasomatic rocks in that isolated systems must always evolve to equilibrium (that is, death) whereas open systems always evolve to one or more non-equilibrium states that can be maintained indefinitely as long as energy and suitable nutrients are added to the system. The other fundamental aspect of open hydrothermal systems is that the mineral reactions that take place within the open "reaction vessel" are invariably *networked* in the sense that one reaction may use the products of another reaction in order to proceed. An example is shown in figure 1.7 where the reaction: muscovite $\rightarrow$ chlorite uses the products from the oxidation of pyrite and the dissolution of ankerite.

[1] A stationary state is a state of a system where some quantity (such as chemical composition or temperature) remains constant and does not change with time. Equilibrium is one such stationary state for a system and linear systems commonly have only one stationary state: equilibrium. Nonlinear systems may have many non-equilibrium stationary states where competing processes balance one another.

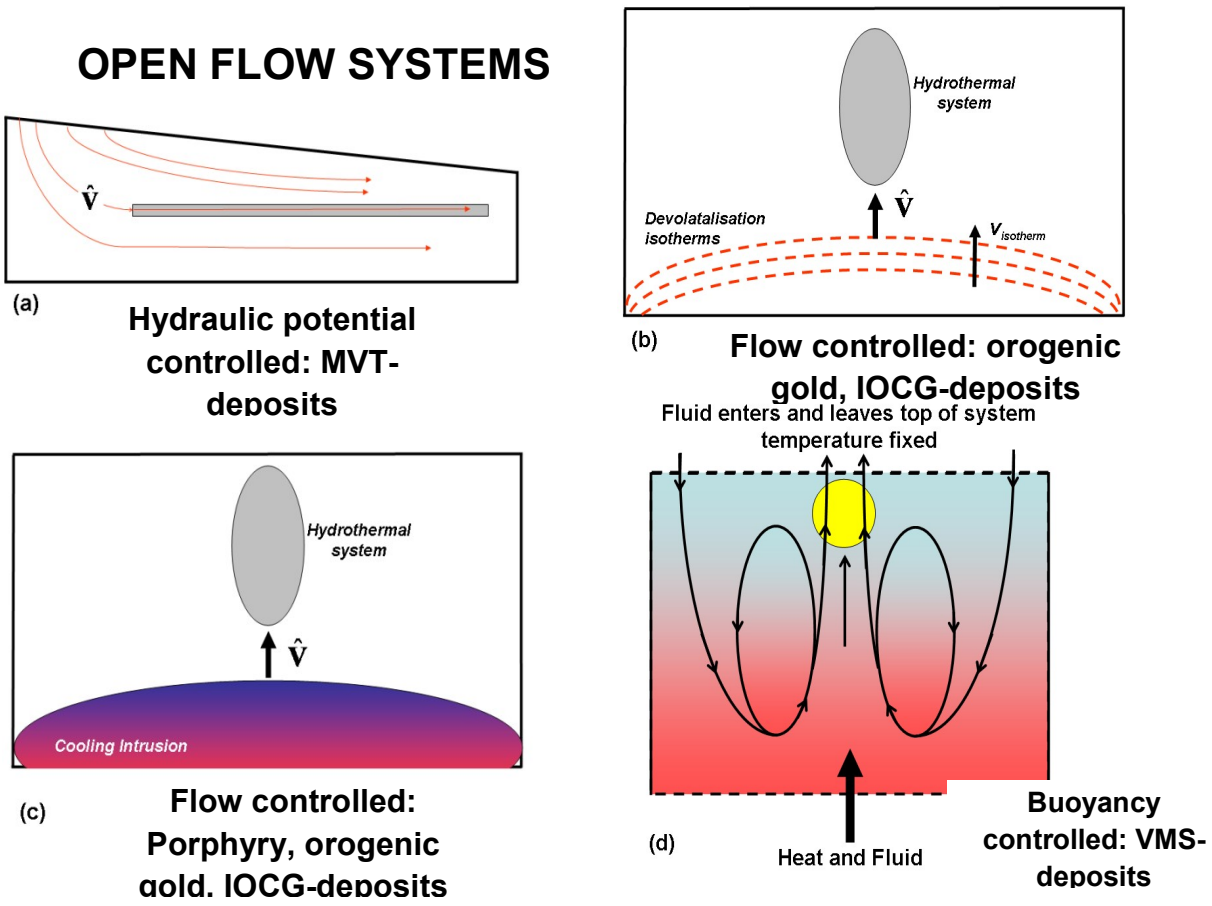



Figure 1.6. Examples of open flow systems. In each case $\hat{V}$ is the constant flux of fluids supplied from the source region (the fuel tank).

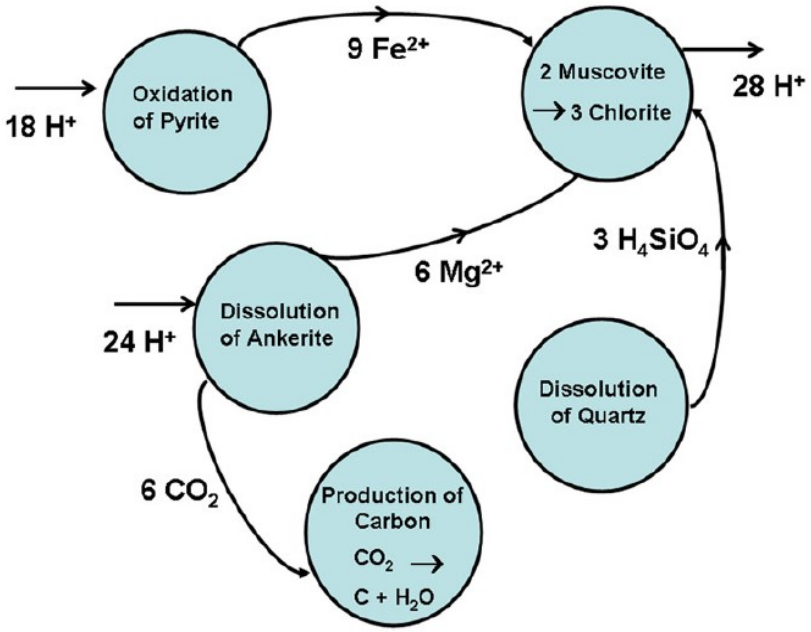



Figure 1.7. Example of a neworked chemical reaction system.

**Table 1** Enthalpies of reaction/mol $H_2O$ ($\Delta H_R$) and relative volume changes ($\Delta V_R/V_{RCT}$) for univariant metamorphic reactions

| Reaction | $\Delta H_R$/kJ/mole $H_2O$ | $\Delta V_R/V_{RCT}$ [%] |
|---|---|---|
| $1Prl + 1H_2O \Leftrightarrow 1Kln + 2Qtz$ | −15.1 | − 0.5 (1) |
| $1Prl + 2And + 5H_2O \Leftrightarrow 3Kln$ | −22.2 | − 7.0 (2) |
| $3Cen + 2H_2O \Leftrightarrow 1Ctl + 1Qtz$ | −32.3 | − 0.1 (7) |
| $1And + 3Qtz + 1H_2O \Leftrightarrow 1Prl$ | −32.9 | − 7.3 |
| $6Fo + 1Tlc + 9H_2O \Leftrightarrow 5Ctl$ | −33.4 | − 4.4 (8) |
| $5Crd + 24H_2O \Leftrightarrow 3Qtz + 8Kln + 2Chl$ | −35.9 | −19.5 |
| $8Tlc + 5Crd + 16H_2O \Leftrightarrow 6Chl + 29Qtz$ | −40.0 | − 7.2 (10) |
| $1Kfs + 1Sil + 1H_2O \Leftrightarrow 1Ms + 1Qtz$ | −44.7 | − 7.4 (11) |
| $4An + 3H_2O \Leftrightarrow 1Kln + 2Czo$ | −46.0 | −18.4 (3) |
| $1Phl + 1Crd + 4H_2O \Leftrightarrow 1Ms + 1Chl + 2Qtz$ | −48.8 | −13.6 (9) |
| $5Tlc + 12An + 10H_2O \Leftrightarrow 3Chl + 6Czo + 17Qtz$ | −49.1 | −11.1 |
| $17Fo + 20An + 28H_2O \Leftrightarrow 5Chl + 3Tlc + 10Czo$ | −58.8 | −13.2 |
| $3Crd + 8H_2O \Leftrightarrow 2Chl + 8And + 11Qtz$ | −59.6 | −17.2 |
| $1Kfs + 4An + 2H_2O \Leftrightarrow 1Ms + 2Czo + 2Qtz$ | −65.4 | −16.1 (5) |
| $4An + 1H_2O \Leftrightarrow 1And + 2Zo + 1Qtz$ | −78.9 | −17.9 (4) |
| $4An + 1H_2O \Leftrightarrow 1Ky + 2Zo + 1Qtz$ | −83.1 | −19.6 |
| $1Adr + 9An + 3H_2O \Leftrightarrow 1Hm + 6Czo + 3Qtz$ | −84.7 | −16.0 (6) |

$\Delta H_R$ and $\Delta V_R/V_{RCT}$ are based on the compilation by Berman (1988, programme update 1992) and refer to standard state conditions 298 K, 100 kPa. $\Delta H_R$/mole $H_2O$ is given for water (liquid). $\Delta V_R/V_{RCT}$ is calculated with respect to the liquid volume of $H_2O$. $\Delta V_R$ – volume of reaction, $V_{RCT}$ – volume of the reactants. – Numbers in brackets refer to the curves in Fig. 1.
An anorthite ($Ca[Al_2Si_2O_8]$); And andalusite ($Al_2SiO_5$); Adr andradite ($Ca_3Fe_2[Si_4O_{12}]$); Cen enstatite ($Mg[SiO_3]$); Chl chlorite ($Mg_5Al[AlSi_3O_{10}](OH)_8$); Crd cordierite ($Mg_2Al_3[AlSi_5O_{18}]$); Ctl chrysotile ($Mg_3[Si_2O_5](OH)_4$); Czo clinozoisite ($Ca_2Al_2O \cdot AlOH[Si_2O_7][SiO_4]$); Fo forsterite ($Mg_2[SiO_4]$); Hem hematite ($Fe_2O_3$); Kfs K-feldspar ($K[AlSi_3O_8]$); Kln kaolinite ($Al_2[Si_2O_5](OH)_2$); Ky kyanite ($Al_2SiO_5$); Ms muscovite ($KAl_2[AlSi_3O_{10}](OH)_2$); Phl phlogopite ($KMg_3[AlSi_3O_{10}](OH)_2$); Prl pyrophyllite ($Al_2[Si_4O_{10}](OH)_2$); Qtz quartz ($SiO_2$); Sil sillimanite ($Al_2SiO_5$); Tlc talc ($Mg_3[Si_4O_{10}](OH)_4$); Zo zoisite ($Ca_2Al_2O \cdot AlOH[Si_2O_7][SiO_4]$)

In addition there are three other fundamental characteristics of hydrothermal mineral reactions:

(i) Most, if not all reactions that produce alteration products (sericite, epidote, chlorite, carbonates, iron oxides) are *exothermic* (Table 1, from Haack and Zimmermann, 1996). Since chemical reaction rates are temperature dependent the alteration process is *self-enhancing* or *thermo-catalytic*. By contrast, reactions involving the precipitation of gold, sulfides and anhydrous silicates such as quartz are endothermic and sap heat from the system; they are *self-terminating*. A qualifying statement is that quartz is commonly produced in the same reaction as produces the hydrous mineral (Table 1) but where the total reaction is exothermic; an example is $1Kspar+4An+2H_2O \rightarrow 1Ms+2Czo+2Qtz$ with the production of 65.4 kJ/mole $H_2O$.

(ii) Many alteration reactions depend on the addition of $H^+$ but produce even more $H^+$ when networked. Thus the oxidation of pyrite in figure 1.7 needs 18 moles of $H^+$ but produces 28 moles of $H^+$ when networked with the muscovite $\rightarrow$ chlorite reaction. Such reactions are said to be *autocatalytic.* Many hydrothermal reactions are autocatalytic with respect to components other than $H^+$. For instance many reactions that produce vein forming minerals have this autocatalytic characteristic particularly those reactions that produce laminated quartz-carbon-chlorite-gold veins typical of orogenic gold deposits and patterned quartz-adularia-gold veins (Henley and Berger, 2000) typical of epithermal deposits.

(iii) Another aspect of mineral reactions in hydrothermal systems is that the replacement reactions are almost universally constant volume in nature rather than taking place under constant pressure conditions as is the common assertion in metamorphic petrology. Thus in figure 1.8 we show an example of sericite plus quartz replacing chlorite in drill core from Sunrise Dam in the Yilgarn of Western Australia. The bedding passes through the replacement with no sign of offset.

Figure 1.8. Constant volume replacement of chlorite by sericite plus quartz. Core from Sunrise Dam Western Australia.

Such constant volume replacement processes have been recognised for at least 100 years by writers such as Lindgren (1912, 1925), Bastin et al. (1931), Ridge (1949) and Merino and Canals (2011). Constant volume replacement demands that the dissolution of the host material equals the growth rate of the pseudomorph. This can mean that the replacement process is self enhancing. The processes are important because many sulfide reactions are constant volume in nature, and if written as constant volume reactions rather than constant mass reactions, become autocatalytic. Ridge (1949) gives many examples of constant volume reactions involving sulfides that are autocatalytic in $\left(SO_4^{2-}\right)$. An example involving 0.92% volume change is (Ridge, 1949, p535):

$$8FeS_2 + 42Fe^{3+} + 77\left(SO_4^{2-}\right) + 14Cu^{2+} + 36H_2O \rightarrow 7Cu_2S + 50Fe^{2+} + 86\left(SO_4^{2-}\right) + 72H^+$$

This reaction converts 77 moles of $\left(SO_4^{2-}\right)$ to 86 moles of $\left(SO_4^{2-}\right)$ and incidentally, also converts 42 moles of $Fe^{3+}$ to 50 moles of $Fe^{2+}$.

The result of any of these characteristics, *networking*, *thermal-* and *auto-catalysis* is that the chemical *systems* become *nonlinear*. This means that the reacting systems can possess many non-equilibrium states and the system can jump from one state to another in a periodic or chaotic manner. In particular the system can jump between oxidised and reduced or high pH/low pH states both in time and space with the attendant oscillatory or chaotic spatio-temporal deposition of gold and sulfides.

All the apparatus developed in *chaos theory* over the past 30 years or so is directly applicable to hydrothermal systems. Just as for systems at equilibrium, the mineral phase assemblages that develop at non-equilibrium steady states are governed by strict thermodynamic rules; these rules resemble, but are not identical to, those developed by Korzhinskii rather than by Gibbs. The assumption of local equilibrium is commonly justified in terms of the systematic order of mineral assemblages observed in metasomatised rock masses. Thus Reed (1997) states: "*The ubiquity of characteristic alteration assemblages….and the rationalisation of such assemblages in thermodynamic terms make it clear that mineral-mineral equilibrium and metastable equilibrium apply on a local scale and can be used to understand the origins of most assemblages*". Such a notion assumes that equilibrium is the only condition that produces systematic order in a chemically reacting system. This is not the case. Just as the change in

Gibbs energy is a function for closed systems and drives the reactions to equilibrium; the *excess work*, Γ, defined by Ross (2008) is a function for both closed and open systems that drives the reactions to a steady state. An open reaction continues at a sationary state until all of the reactants are consumed when the reaction stops; it never reaches equilibrium yet the product is characterised by the value of the chemical potential. Γ is a state function and is an extremum at all stationary states; $\Gamma \geq 0$ for a displacement from a stationary state. The equivalent statements for the Gibbs energy difference, ΔG, are that ΔG is an extremum at equilibrium and $\Delta G \leq 0$ for a displacement from equilibrium. For a discussion of the excess energy see Ross (2008) for application to chemical systems and Velarde (1996) for application to thermal and viscously deforming systems.

Thus since Γ defines an ordered approach to a stationary state and involves the chemical potential of the phases being produced there is no reason why systematic order in mineral assemblages should not characterise stationary states far from equilibrium just as it does equilibrium states. This conclusion is reinforced by examining the phase rule for non-equilibrium systems. The concept of a phase rule also applies in the case of a system at a stationary state just as it does for a system at equilibrium (Callen, 1960) or an open system (Korzhinskii, 1950, 1965, 1966, 1967). The phase rule is simply a statement of the number of known (or fixed) quantities and the number of unknown quantities in a chemical system. As such it defines the number of independent degrees of freedom, *f*, available to any chemical system defined by a number of mineral phases, *M*, and molar fractions, $r_k$, of *k* chemical components. *f* can be defined for any system depending on the constraints on *M* and $r_k$; $\sum_{n=1}^{k} r_n = 1$. For a system at equilibrium there are *r*(*M* - 1) equations defining the relationships between the chemical potentials for each chemical component in the phases *M* and a set of [2 + *M*(*r* - 1)] independent variables corresponding to T, P and the (*r* - 1) independent mole fractions. Thus $f = r - M + 2$ for an equilibrium system. Korzhinskii (1966, 1967) points out that for open flow systems there is a set of chemical components (called *mobile* components) where the chemical potentials are fixed outside of the system. This reduces the number of independent chemical potentials and hence reduces *f* so that the resulting mineral assemblages tend to be smaller in number than those developing in closed metamorphic systems. These arguments of Korzhinskii are quite general and do not depend on an appeal to *local equilibrium*. In a similar fashion the fact that the chemical potentials at a stationary state are fixed by the concept of *excess energy* (Ross, 2008) and are not independent means that *f* is again reduced from the equilibrium value and so the number of phases coexisting at a stationary state will be smaller than at equilibrium.

Thus open flow hydrothermal systems are giant chemical reaction vessels within which a variety of nonlinear processes operate and which are held far from equilibrium so long as energy and nutrients are added to the system. However there is one more fundamental aspect of the behaviour of these reaction vessels that is responsible for the evolution of these systems and controls whether the system is successful in producing an ore body or fails.

In order to accommodate the imposed fluid flux the system must evolve through a number of modes of operation as (i) the initial reactants within the vessel are used up; (ii) depositing

minerals clog up the porosity and (iii) the fluid flux changes due to variations in fluid viscosity, density and/or supply of fluid.

If the fluid flow is driven by the gradient in hydraulic head, e.g. Mississippi Valley type deposits, then if the flow is through pores of the rock and is slow, with viscosity, μ, then the fluid flux per unit area, $\hat{V}$, for a given imposed gradient in the hydraulic head, $\nabla\mathcal{H}$, is controlled by the current permeability, K, through what is known as Darcy's Law:

$$\text{fluid flow velocity} = \frac{\text{permeability}}{\text{viscosity x porosity}}(\text{gradient in hydraul ic head})$$

$$\hat{V} = \frac{K}{\mu}\nabla\mathcal{H}$$

where μ is the fluid viscosity. This is a strong function of temperature and pressure (Figure 1.9). Here permeability is the critical factor. If the porosity clogs up the system shuts down. Successful systems display evidence of processes that maintain the permeability such as the formation and/or enhancement of porosity by self-enhancing chemical processes that are invariably expressed as pseudomorphic microstructures with widespread compositional zoning of mineral grains (Merino and Canals, 2011).

If the fluid velocity is fixed (as in orogenic gold or porphyry copper deposits) the permeability has to continuously adjust to accommodate the imposed flow, and Darcy's Law is rewritten as:

$$\text{permeability} = \frac{\text{fluid flux x viscosity}}{(\text{gradient in hydraulic head})}$$

$$K = \frac{\hat{V}\mu}{\nabla\mathcal{H}}$$

Here fluid flow is the dominating control on the system. For instance, if the fluid flux is fixed at the input to the system and the viscosity increases due to a slight change in temperature or fluid pressure then the permeability must adjust. Commonly some form of fracturing is the only way of achieving this rapidly. Thus these deposits show evidence of accommodating adjustments in the form of fractures, veins, breccias and stock-works.

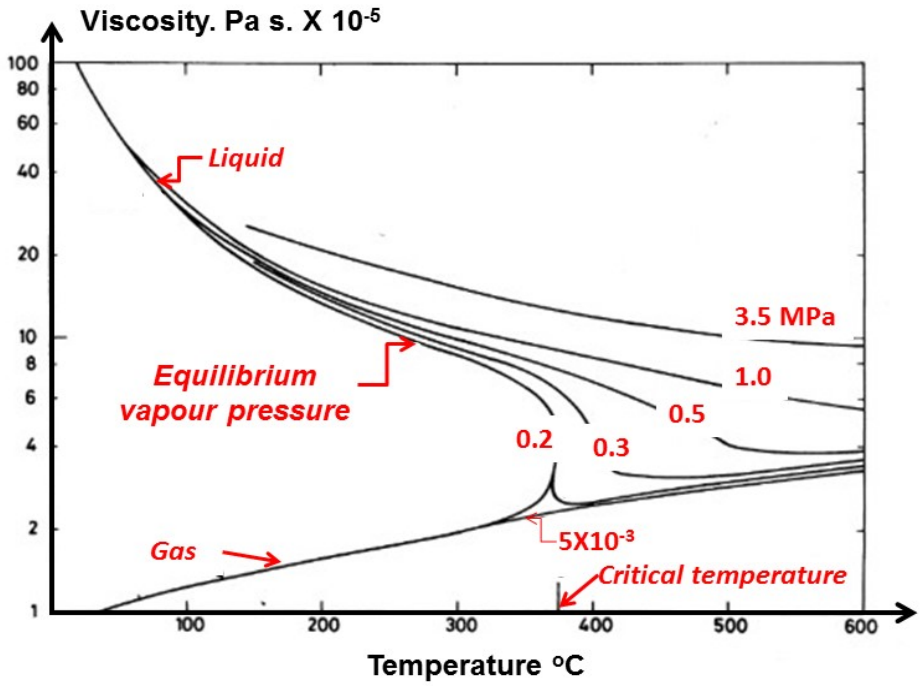



Figure 1.9. Variation of the viscosity of pure water with temperature. Modified after Barnes (1997).

Successful hydrothermal systems accommodate these changes by (i) switching from pervasive exothermal alteration of feldspars and mafic minerals to form sericite, carbonates and iron oxides to competing, localised exothermic/endothermic mineral reactions such as chlorite and biotite competing with sulfide, gold and quartz deposition; (ii) localised brecciation and/or vein development; (iii) simultaneous, episodic dissolution and deposition of carbonates, silicates and sulfides to generate porosity (especially in MVT deposits). All of these switches can be read from microstructural studies and from the paragenetic sequence (Figure 1.10).

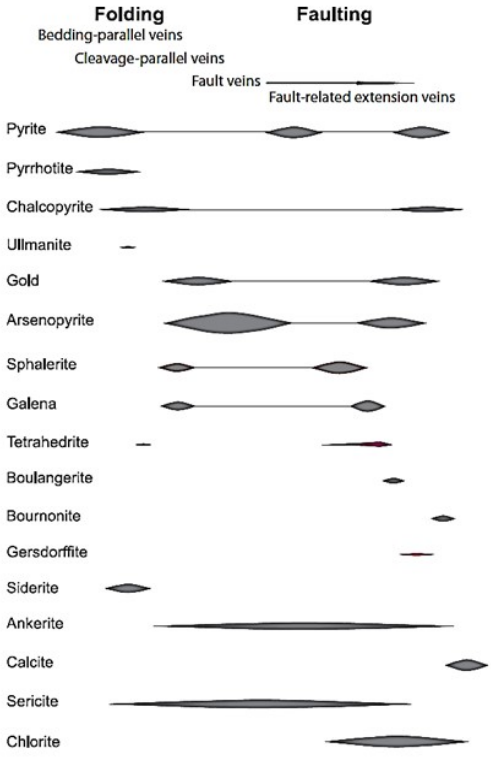


Figure 1.10. Paragenetic sequence correlated with deformational events. Bendigo gold system. From Wilson et al. (2012).

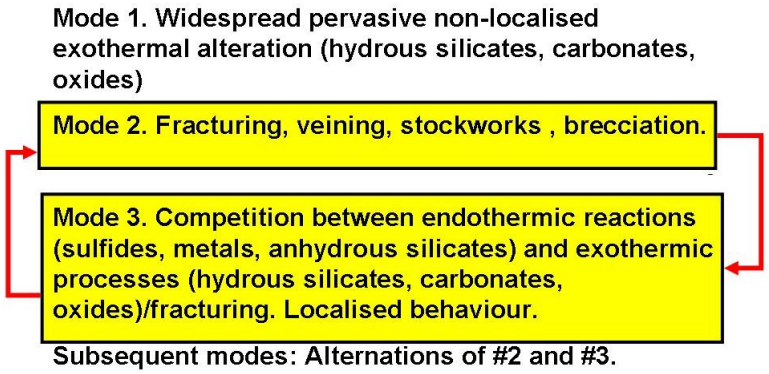



Figure 1.11. The modes of operation of a flow controlled reactor.

Successful hydrothermal systems therefore pass through the following modes of operation as shown in Figure 1.11: *Mode 1:* a one-off initial extensive, non-localised pervasive alteration characterised by exothermal mineral reactions to produce sericite, epidote, carbonates and iron oxides. The imposed fluid flux is accommodated by the exothermic nature of the reactions. *Mode 2:* When the initial reactants (feldspars and mafic minerals) are exhausted the system must switch to a new mode of operation to accommodate the imposed flow. This commonly involves localised brecciation and/or vein formation both of which are very efficient ways of increasing or maintaining the permeability. The veins are internally structured and appear as laminated or internally patterned veins. The processes that produce the laminations and/or patterns are an intrinsic part of the deposition of sulfides and gold. *Mode 3:* This fracturing mode is followed immediately by competition between endothermic mineral reactions (gold, sulfides, anhydrous silicates) and exothermic reactions (chlorite, biotite, iron oxides). If this competitive mode does not develop the system dies. *Mode 4:* Really successful systems are characterised by a large number of cycles through Modes 2 and 3. We emphasise that these mode switches and the detailed nature of the veins and breccias that form are controlled solely by the *nonlinear* nature of the mineral reaction systems coupled to fluid transport. We discuss these particular processes in detail in Chapter 8.

## 1.2. Understanding and quantifying the irregularity and unpredictable nature of mineralising systems.

A characteristic of many natural systems, such as the development of turbulence in fast flowing fluids, is that the driving forces that cause the system to evolve are imposed at a large length scale but the dissipative processes operate at smaller length scales. Thus as indicated in Figure 1.1, in hydrothermal systems the driving forces may be imposed at length scales measured in thousands of kilometres whereas the dissipative processes may operate down to the nanometre scale. The interval between the scale where forcing occurs and the smallest dissipative scale, is called the *inertial interval*, or the *transparency window*. For hydrothermal systems the inertial interval covers at least 15 orders of magnitude.

In natural nonlinear systems where the forcing processes operate at a large length scale and the dissipative processes operate at smaller scales the energy transfer occurs across the scales by a

*cascade* process whereby processes operating at large length scales shed energy to processes operating at smaller length scales until finally at small scales the dissipation is negligible or processes (such as endothermic mineral reactions) operate that consume energy. This process is expressed in the famous poem by Richardson (1922) regarding turbulent flow in the atmosphere:

*Big whirls have little whirls*
*Which feed on their velocity,*
*And little whirls have lesser whirls*
*And so on to viscosity.*

In general the cascade process in hydrothermal systems is towards smaller length scales so that large ore bodies are always associated spatially with a cascade of ever smaller mineralised packages. Such a cascade process to smaller and smaller length scales is called a *direct cascade* and one example is cataclasis or brecciation where both mass and energy are transferred to smaller and smaller scales. For mineralised hydrothermal systems one might write, paraphrasing Richardson:

*Big ore bodies have little ore bodies*
*The result of criticality,*
*And little bodies have lesser bodies*
*And so to multifractality.*

We develop the details associated with this ditty throughout the book. In Figure 1.12(a) the mineralised packages are shown as regular geometrical features and the same geometry is repeated at smaller length scales so that the system is self-similar. Clearly this is not the case in nature and considerable irregularity in spatial distribution is generally observed as presented in Figure 1.12 (b). In some systems such as turbulent fluid flow this irregularity is called *intermittency.* Intermittency is a characteristic of most naturally occurring systems and is a particular feature of the distribution of gold in orogenic gold systems.

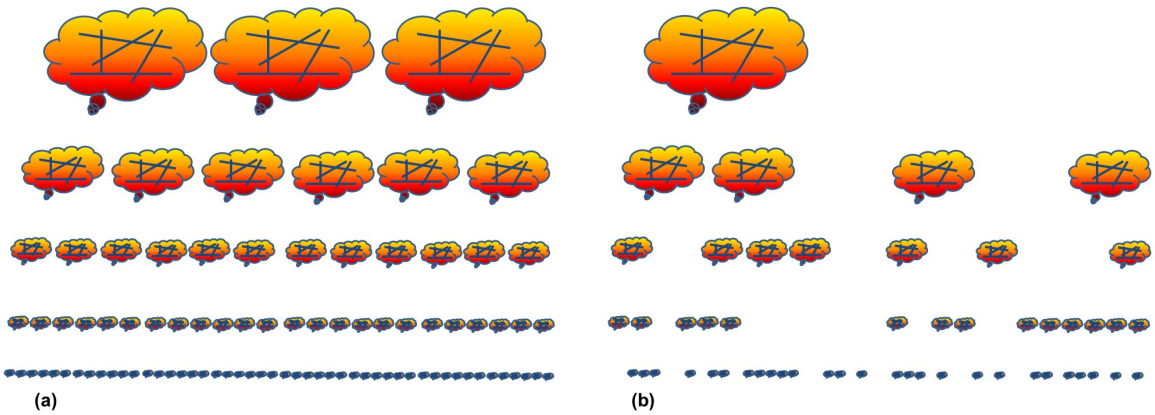



Figure 1.12. Fractal size distribution of ore bodies. (a) A fractal self-similar distribution. (b) A fractal distribution with intermittency.

However cascade processes can operate from small to larger scales in some natural systems. This is called an *inverse cascade* and a natural example is the agglomeration of water drops to form a cloud or the agglomeration of rain drops on a widow pain to form a rivulet. Another example is the case of metamorphic systems where the progressive agglomeration of partial

melt ultimately forms a pluton. Here both energy (in the form of latent heat) and mass are cascaded to larger and larger scales. A very similar example of an indirect cascade is the formation of a large hydrothermal mineralised system where fluxes of heat and fluids are progressively focussed into a single highly reactive site where metals are concentrated to levels up to $10^4$ above background levels. With apologies to Richardson:

*Small concentrations grow to big concentrations*
*That feed on energy advection,*
*Big concentrations grow to larger concentrations*
*And so to explorers' satisfaction.*

In view of the extreme spatial and temporal irregularity commonly observed in hydrothermal ore bodies, highly relevant questions are: *Is all this irregularity purely random? Or do these systems follow some kinds of rules? And is it possible to make some sense out of all the irregularity?* In anticipation of the remainder of this book the answers to these questions are no, yes and yes, but we need to develop some new tools in order to discover the beauty in the systematics inherent in this behaviour.

In order to give some feel for the answers to these questions we look at a very simple system that has many of the irregular characteristics of mineralising systems. We view hydrothermal systems as dynamical systems (those that evolve with time) and, as such, distinguish two end-member types of dynamical systems. One is a deterministic system in which the future state of the system is determined by the nature of some previous state according to some mathematical formula. The other is a stochastic system where the future state of the system is defined by some random process such as the toss of a coin. We consider hydrothermal systems to be governed by the laws inherent in the behaviour of physical and chemical systems and hence are deterministic dynamical systems. Such systems show a variety of behaviours and can exhibit chaotic behaviour (that is, sensitivity to initial conditions) if the mathematical relations involved in defining the evolution of the system are nonlinear.

One characteristic of the evolution of hydrothermal systems is that they can be considered to be iterative systems. That is, the state of the system at one instant depends on the immediately previous state in time. An example is the evolution of permeability where the permeability at one instant depends on the value in a previous instant. An additional characteristic, as illustrated in figure 1.2, is that this dependency on a previous state may depend on other processes that operate in the system so that there is feedback between different simultaneous processes. We first consider a system where there is no feedback and the value of some quantity, such as the concentration of some species, A, at time $t = n+1$, $A_{n+1}$, depends solely (in a linear manner) on the concentration at time $t = n$:

$$A_{n+1} = \alpha A_n \qquad (1.1)$$

where $\alpha$ is a constant. Expressions such as (1.1) are an example of a discrete dynamical system and such relations are useful in trying to understand complex systems where the real mathematical equations are difficult, or perhaps impossible, to solve. If we assume for example that $\alpha = 2$ and start with, say $A_n = 0.1$, then we can calculate $A_{n+1}$ at all future times using an Excel spreadsheet. This and similar examples are fun to do and explore on a rainy,

cold Sunday afternoon. The first 20 entries in this evolution are shown in figure 1.13 (a) below and plotted in Figure 1.13 (b).

Figure 1.13 (a and b) represents a system that grows with no competition and depends only on its previous state; it simply grows exponentially. However, as we have seen above, the characteristic feature of systems not at equilibrium is competition between processes. So, let us now write an expression that embodies competition;

$$A_{n+1} = \alpha A_n \left(1 - A_n\right) \qquad (1.2)$$

The first part of the right hand side of this expression, $\alpha A_n$, expresses exponential growth as we have seen. The second part, $-\alpha A_n^2$, expresses the fact that some of A is being used in another process (such as another mineral reaction) so now there is competition for the growth of A. Now if we run our spreadsheet, with $\alpha$ = 3, we get Figure 1.13 (c and d). The system now evolves to periodic behaviour with two slightly different wavelengths present.

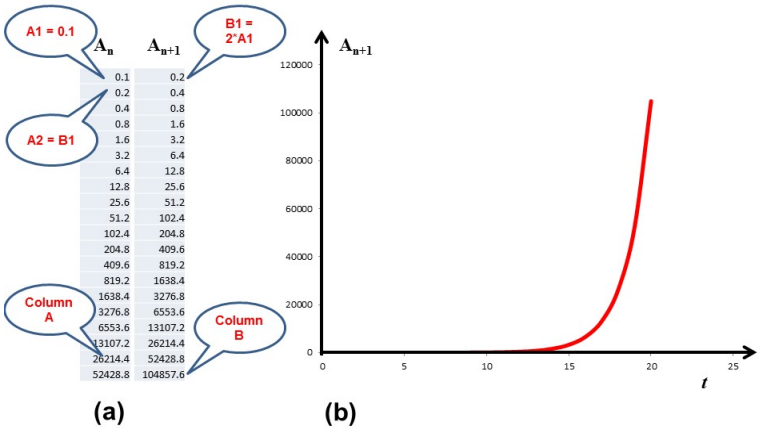
If we now increase A to 4 still with the initial value of A = 0.1 we obtain the blue curve in Figure 1.13 (e) where the first 30 steps are plotted. The resulting behaviour is now non-periodic and in fact is quite irregular. Some might call the behaviour random but in fact the behaviour is clearly deterministic since we can easily say what the behaviour will be between say steps 1000 and 1030 by running our Excel spreadsheet.

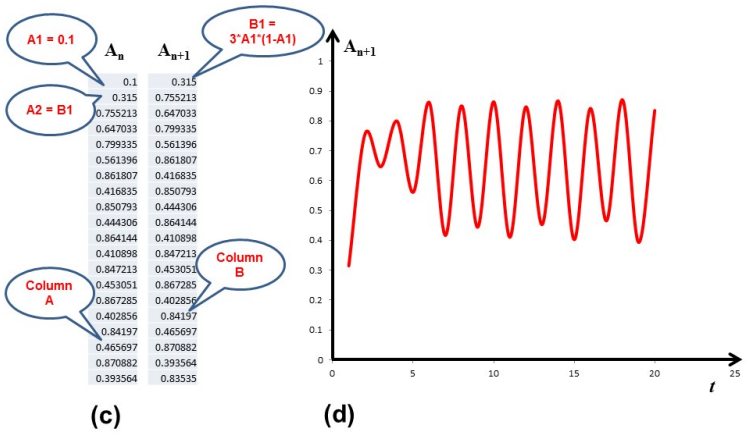
There is an additional fundamental aspect to the behaviour of this system for $\alpha$ = 4. If we change the initial value of A by 0.1% from 0.1000 to 0.1001 and run our spreadsheet again, we obtain the red curve in Figure 1.13 (e). This duplicates the behaviour of the system for the first 5 or so steps but then begins to diverge so that by 30 steps there appears to be no correlation in behaviour even though both the blue and red curves are completely deterministic. This sensitivity to initial conditions is formally known as *chaos*. This sensitivity to initial conditions is also demonstrated by changing $\alpha$ in (1.2) by a small amount. As an exercise, figure 1.13(f) below results for $\alpha$ = 3.8. As a spectacular exercise the reader should decrease $\alpha$ by 13.6 % and try $\alpha$ = 3.284.

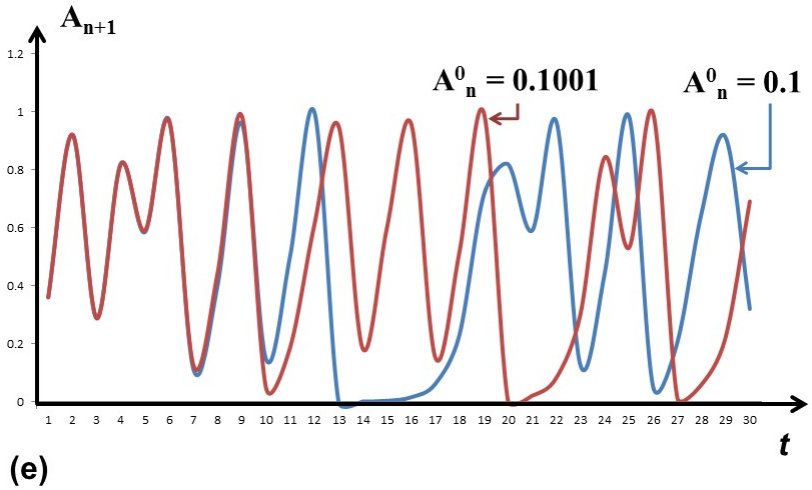
The simple system described by (1.2) exhibits one other important form of behaviour, *intermittency* with apparently irregular bursts of activity. If we run our spread sheet again with initial conditions $A_0$ = 0.2 and with $\alpha$ = 3.8 we obtain figure 1.13 (f). Further aspects of the behaviour of (1.2) which is called the *logistic equation* (Sprott, 2003) and the behaviour of other similar systems are considered in Chapter 5.

Although the signal in Figure 1.13 (f) is irregular, one can extract fundamental information from the signal by a very simple construction called a *return map* (Sprott, 2008). We simply plot the value of the signal at $n$ = 1 against the value at $n$+1 and repeat the procedure. So the next point is obtained by plotting $A_{n+1}$ against $A_{n+2}$ and so on. The result is Figure 1.13(g) which is the *attractor* for the signal in Figure 1.13(f). This is none other than the plot of (1.2). Thus the underlying iterative process that produces the irregular signal in Figure 1.13(f) can be extracted from the data by constructing a return map.

Notice by zooming into Figure 1.13 (g) that the return map has structure within it. Thus the attractor for this system is fractal. A fractal attractor is called a *strange attractor*. The return map for a random signal shown in Figure 1.13 (i) is given in Figure 1.13 (h). The clear randomness of the signal is revealed by the return map.



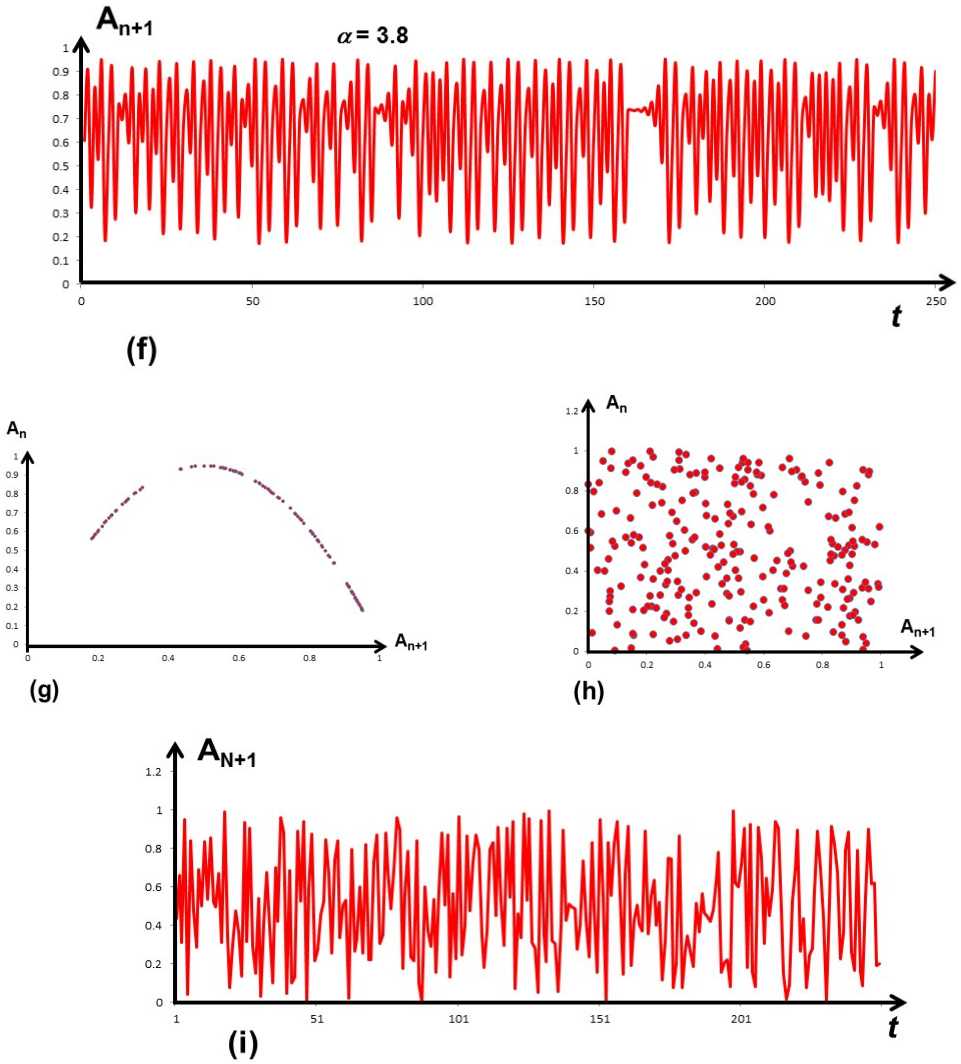



Figure 1.13. Some aspects of iterative behaviour. (a) A system with no competition to growth given by (1.1). This represents the two columns A and B of a spreadsheet with the formulae entered to calculate the iterations described by (1.1). The result is exponential growth as shown in (b). (c) The spreadsheet for the iterative scheme given in (1.2) with $\alpha = 3$ and the initial value of A = 0.1. (d) The behaviour of the iterative scheme with time. The response is close to periodic with two wavelengths of similar amplitude. (e) The behaviour of (1.2) with $\alpha = 3.0$. For the blue curve the initial value of A is 0.1000; for the red curve the initial value of A is 0.1001. This figure demonstrates the sensitivity of the system to initial conditions. (f) Intermittent (burst or clumping) behaviour of the logistic system over the first 250 steps with $A_0 = 0.2$ and $\alpha = 3.8$. (g) Return map for data in (f). (h) Return map for data in (i). (i) Random numbers between 0 and 1 generated using Random Number Generator in Excel.

## 1.3. A new paradigm for hydrothermal mineralising systems.

A new paradigm for understanding hydrothermal mineralising systems is built around the following five propositions:

1. Hydrothermal systems are open flow chemical reactors that remain far from equilibrium in mechanical, hydrological, thermal and chemical terms for as long as nutrients and energy are fed to the system. The size and grade of the deposit is a function of the time that they remain open and the efficiency of the networked processes that operate within the reactor. The open flow nature of the systems coupled with feedback relations between chemical-mechanical-hydrological-thermal processes leads to system behaviour that is

episodic or chaotic where the term chaotic is used to indicate that the system behaviour is sensitive to initial conditions. Thus no two ore systems are identical, they show irregular distributions of structure, alteration and mineralisation and preserve a paragenetic sequence. These are all the hallmarks of non-equilibrium, chaotic systems.

2. Hydrothermal systems are critical systems where the term *critical* is meant in the classical sense of the word rather than in the sense of *self-organised criticality*. This means that a critical system is one that undergoes a phase transition where a homogeneous, structure-less system develops structure at a number of spatial and temporal scales with well-defined scaling laws and where intermittency and long range correlations exist. The problem in such systems is to understand these scaling laws and the physical-chemical processes responsible for them.
3. Since these systems are open throughout their life the model: *source-transport-trap* gives an incorrect conceptual view of the evolution of such systems and thus provides concepts that can be misleading. Thus the idea that domes or anticlinal hinges provide concentration sites for fluids is completely misleading in an over-pressured system with the hydrological constraint of continuous fluid flow. A better analogue would be with a chemical reactor such as an internal combustion engine where the system of interest is described by: *fuel tank(s)-fuel line(s)-reaction site*.
4. The sources for alteration fluids (*the fuel tanks*) are far better constrained than perhaps 5 years ago. The thermodynamic constraints on sources of $CO_2$, K-rich and Na-rich fluids within the lithosphere are much better defined now and provide clear exploration concepts that enable more precise questions to be asked.
5. Even though system behaviour is chaotic, well defined procedures exist to describe, characterise and analyse such systems. These procedures are grounded in the physics and chemistry of the processes that operate and are inherently more robust and useful from an exploration sense than existing empirical, pattern recognition or statistical procedures.

We consider various aspects of this open flow chemical reactor, critical approach in the remainder of this book.