Chapter_12
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12.1. Introduction.

In this chapter we examine the repercussions of coupling deformation and mineral reactions in an open flow hydrothermal system. The result is large amplitude oscillations in temperature and fluid pressure which in turn lead to large oscillations in the equilibrium solubility of gold and of vein filling minerals such as quartz and carbonates. We discuss a model for the deposition of gold in such systems and the resultant controls on ore grade.

Many previous workers have recognised episodic behaviour in hydrothermal systems. Examples are crack-seal veins (Cox and Etheridge, 1983; Fisher and Brantley, 1992), laminated quartz veins (Chase, 1949; Vearncombe, 1993), compositional zoning in minerals (Thomas et al., 2011) including gold (Butt and Timms, 2011), multiple overprinting brecciation events (Boullier and Robert, 1992; Oreskes and Einaudi, 1990), and fluid inclusion histories (Wilkinson and Johnson, 1996). Mechanisms for driving such episodic behaviour are commonly proposed to arise from pore fluid pressure fluctuations associated with adiabatic seismic events and associated fault-valve behaviour or suction pump/piston processes (Sibson, 1987, 1995, 2001, Boullier and Robert, 1992; Cox, 1995, 2005; Henley and Berger, 2000; Weatherley and Henley, 2013; Sanchez-Alfaro et al., 2016; Cox, 2016). These mechanisms call for catastrophic fluid depressurisation (Weatherley and Henley, 2013) and resulting adiabatic deposition of gold by phase separation processes (Simmons and Brown, 2006). One might call such mechanisms *extrinsic* since they rely on the activity of processes outside the hydrothermal system associated with crustal scale deformations. In this chapter we emphasise that hydrothermal systems are unstable dynamical systems and that *intrinsic* processes (aseismic chemo-thermal-deformation processes operating entirely within the system) result not only in fluctuations in pore pressure but also in large excursions in temperature with resultant influences on localised gold deposition. These events are orders of magnitude slower than seismic events and probably overlap the time scales for slow earthquakes. The resulting pore pressure drops are non-adiabatic and are associated with large temperature drops. Some aspects of intrinsic episodic processes have been considered by Henley and Berger (2000).

Since hydrothermal systems evolve both spatially and temporally they are dynamical systems and since they are open to the input of fluids, heat and chemical components they are non-equilibrium dynamical systems. The processes that operate within these systems are nonlinear and inter-related; examples are the exponential dependence of reaction rates on temperature, dependence of the activation energy of a reaction on pH, the competition between diffusion of fluids to or away from reaction sites and the production of fluid at a devolatilising site, and the production of heat from brecciation and exothermic chemical reactions and its coupling to fluid pressure and chemical reaction rates. Thus hydrothermal mineralising systems are nonlinear, non-equilibrium dynamical systems and in this chapter we consider some aspects of the nonlinear dynamics of such systems.

Mineralising hydrothermal systems associated with orogenic gold deposits evolve with time. Two modes of operation can be distinguished. The first is an exothermic, fluid absorbing phase with the pervasive development of hydrous silicates such as sericite and chlorite and of carbonates such as calcite, ankerite and siderite from anhydrous phases such

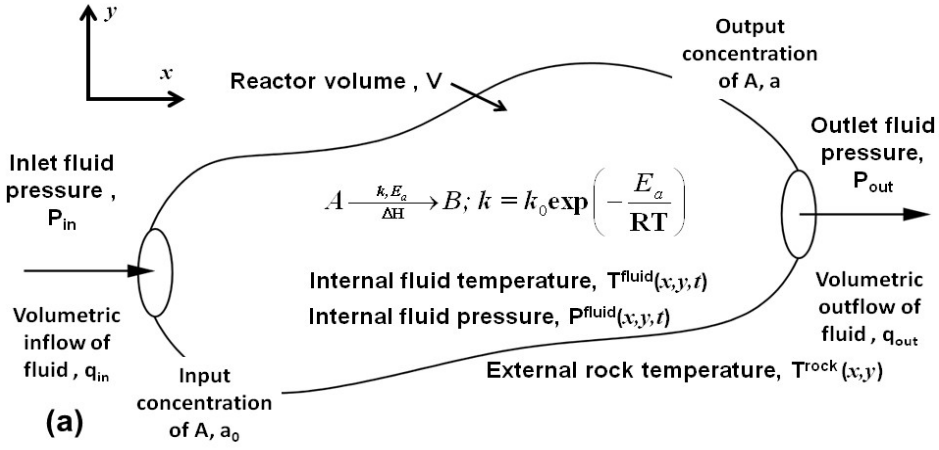
as pyroxenes and feldspars. This stage may or may not be associated with weak mineralisation. The second mode is more localised and typically higher in temperature than mode I. Mode II is characterised by competition between exothermic processes (such as fracturing, brecciation, stock-work formation and veining) and endothermic processes such as dehydration or decarbonisation of previously formed alteration assemblages, and the deposition of metals such as gold. Anhydrous silicates such as epidote or K-feldspar may form at this stage and typically the processes release fluids previously bound in hydrous or carbonate alteration assemblages during mode I. Mode II is noticeably episodic with many (100's to 1000's) overprinting events recorded as multiple stages of brecciation, crack-seal microstructures, laminated veins, compositional zoning in minerals, fluid inclusion compositions and multiple stages of gold deposition, and sometimes, gold dissolution (Cameron, 1998) and remobilisation (Fougerouse et al., 2016). For examples of these modes of operation in hydrothermal systems see Oreskes and Einaudi (1990), Wilkinson and Johnson (1996), Barnicoat et al. (1997), Henley and Berger (2000), Baker et al. (2103), Wilson et al. (2009, 2013), Schaubs and Zhao (2002), and Zhu et al. (2011).

12.2. Orogenic gold systems as open flow chemical reactors.

The essential ingredient for the formation of an orogenic gold hydrothermal system is the influx of hot fluids bearing chemical components such as CO_2, H^+, H_2S and Au. The distribution of such fluids within the system is influenced by local variations in fluid pressure which arise from the distributions of temperature, permeability and of mechanical and chemical dilatancy. The flow itself adds energy to the system in the form of heat and momentum and creates the chemical environment for alteration and mineralising reactions to proceed. Since the mineral reaction rates are a sensitive function of fluid supply the spatial distribution of fluid flow rates becomes a critical issue for the development of the system. In this section we consider some aspects of open flow systems, in particular, the control of mineral reaction rates by the supply of fluids and heat together with controls on the equilibrium solubilities of gold and quartz and on the deposition of gold and quartz.

12.2.1. The models considered in this chapter.

In order to emphasise the essential features of orogenic gold hydrothermal systems we idealise the processes involved in Figure 12.1.



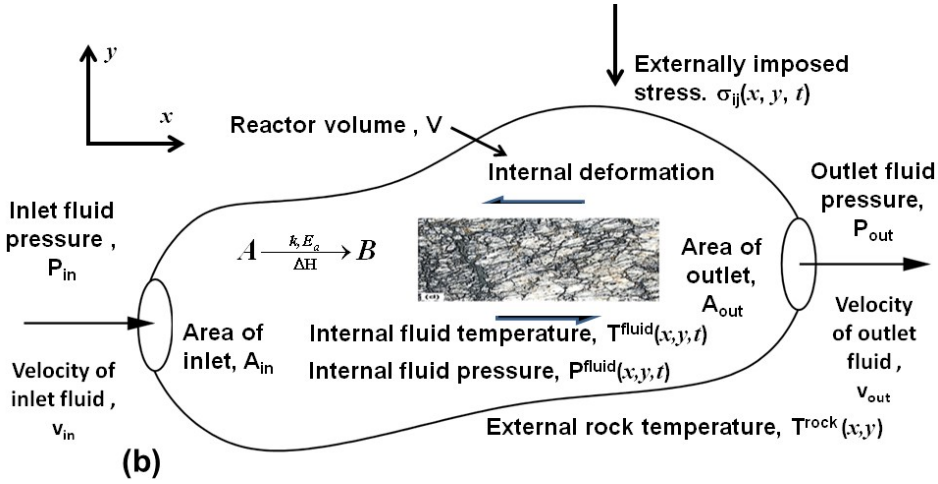


Figure 12.1. The two idealised end-member hydrothermal systems considered in this chapter. The systems are open flow chemical reactors with volume, V. The inlet and outlet areas of the system are A_{in} and A_{out} with inlet and outlet fluid flow velocities v_{in} and v_{out}. This means we can define inlet and outlet fluid fluxes as $q_{in} = v_{in}/A_{in}$ and $q_{out} = v_{out}/A_{out}$. The inlet fluid pressure is P_{in}. Darcy's law, the value of q_{in} and the presence of internal sources and sinks of fluids then establish the local fluid pressure, P^{fluid}, as a function of the spatial coordinates, x, y and of time, t. These relationships then establish the outlet fluid pressure and fluid velocity, P_{out} and v_{out}. Mineral reactions occur within the reactor one of which is $A \xrightarrow[\Delta H]{k,E_a} B$ with rate constant, k, and enthalpy of reaction, ΔH. In general k depends on the absolute temperature, T, through $k = k_0 \exp\left(-\frac{E_a}{RT}\right)$ where k_0 is a reference rate, E_a is the activation energy and R is the gas constant. This reaction also has an associated volume change, ΔV and may or may not produce fluids. The external rock temperature is T^{rock} which is a function of x and y. Internal deformation occurs under the influence of externally imposed stresses, σ_{ij}, also a function of x, y and t. Heat liberated from these deformations and from chemical reactions combines with the temperature of the incoming fluid and diffusion of heat through and from the system to produce an internal temperature distribution, $T^{fluid}(x, y, t)$. Fluctuations in temperature combined with episodic release of fluid from mineral reactions also lead to fluctuations in fluid pressure, $P^{fluid}(x, y, t)$. (a) A system that is not deforming with a single exothermic mineral reaction that does not produce fluids. (b) A deforming system in which the deformation (brecciation and fracturing) is exothermic, coupled to a mineral reaction that may be endothermic and producing fluids. Figures modified substantially from Rawlings and Ekerdt (2013, Figure 6.2).

We consider an open flow system (Figure 12.1) which comprises a chemical reactor with volume, V. The inlet and outlet areas of the system are A_{in} and A_{out} with inlet and outlet fluid flow velocities v_{in} and v_{out}. Thus the inlet and outlet fluid fluxes (with units $m^3s^{-1}m^{-2}$) are $q_{in} = v_{in}/A_{in}$ and $q_{out} = v_{out}/A_{out}$. The inlet fluid pressure is P_{in}. Darcy's law, the value of q_{in} and the presence of internal sources and sinks of fluids then establishes the local fluid pressure, P^{fluid}, and gradients in P^{fluid} as a function of the coordinates, x, y and of time, t, together with the outlet fluid pressure and fluid velocity, P_{out} and v_{out}. Mineral reactions occur within the reactor, one of which is $A \xrightarrow[\Delta H]{k,E_a} B$ with rate constant, k, and enthalpy of reaction, ΔH; k depends on temperature through an Arrhenius relation, $k = k_0 \exp\left(-\frac{E_a}{RT}\right)$, where E_a is the activation energy for the reaction, R is the gas constant and k_0 is a reference rate. Some reactions are endothermic and remove heat from the system and some are exothermic and add heat to the system. These reactions also have an associated volume change, ΔV and may or

may not produce fluids. Reactions that produce hydrous or carbonate silicates from anhydrous or un-carbonated silicates remove fluids from the system. Reactions that produce anhydrous silicates from hydrous assemblages add fluids back into the system. The external rock temperature is T^{rock} which is a function of x and y. Internal deformation occurs under the influence of externally imposed stresses, σ_{ij}, also a function of x, y and t. Heat liberated from these deformations and from chemical reactions combines with the temperature of the incoming fluid and diffusion of heat through and from the system to produce an internal temperature distribution that is a function of both space and time, $T^{fluid}(x, y, t)$. Fluctuations in temperature combined with episodic release of fluid from mineral reactions also lead to temporal and spatial fluctuations in fluid pressure, $P^{fluid}(x, y, t)$. The energy balance of the system is given by

$$\begin{bmatrix} Rate\ of\ energy \\ accumulation \end{bmatrix} = \begin{bmatrix} Rate\ of\ energy \\ entering\ system \\ by\ inflow \end{bmatrix} - \begin{bmatrix} Rate\ of\ energy \\ leaving\ system \\ by\ outflow \end{bmatrix} + \begin{bmatrix} Rate\ of\ heat\ added\ to\ or\ removed \\ from\ the\ system\ by\ diffusion \end{bmatrix} + \begin{bmatrix} Rate\ of\ work \\ done\ on\ and\ in\ the\ system\ by \\ internal\ deformation \end{bmatrix} + \begin{bmatrix} Rate\ of\ heat\ added\ to\ or\ removed \\ from\ the\ system\ by\ internal\ mineral\ reactions \end{bmatrix} \tag{12.1}$$

A fundamental assumption is that the time scale for the operation of these systems is less than ≈ 1 million years (see Chapters 2 and 8) so that the rates of heat production from exothermic mineral reactions and from deformation exceed background crustal radiogenic heat production rates. Later in this chapter we examine aspects of the energy balance in (12.1) and show that, in general, the system is unstable and oscillates indefinitely as long as energy is added to the system and suitable reactants exist within the system. Initially however, since the mineral reaction rates are sensitively dependent on the supply of fluids and heat, we need to clarify the influence of such supply issues on the rates of mineral reactions.

12.3. Principles involved in coupling of processes in hydrothermal systems.

12.3.1. The coupling between the supply of heat and nutrients to mineral reaction rates.

In Chapter 8 we showed that the behaviour of open flow chemically reacting systems is intrinsically different to that of thermodynamically closed systems. In closed systems the kinetics of a chemical reaction depends solely upon the rate constants for the reaction and the system must ultimately monotonically approach equilibrium. In open systems the rate constants also play a role in defining the kinetics but the rate of a chemical reaction also depends on the rates of supply (and removal) of heat and nutrients for the reaction. If the reaction rate outstrips the net supply of either heat or mass then the reaction stops until the supply can build up again.

Thus, open system behaviour is typically episodic and the system remains far from equilibrium for as long as energy and mass are added to the system. Multiple non-equilibrium stationary states can exist, some of which are stable and others unstable. The system can switch from one stationary state to another or evolve from one state to another depending on the supply of energy and mass. The episodic behaviour of chemical reactions is characterised by an *ignition temperature* where the reaction rates become significant and an *extinction temperature* where the reaction rates become insignificant. These temperatures for a particular reaction depend on the activation energy for that reaction. In fact the paragenetic sequence in a particular hydrothermal system is a reflection of the sequence of ignition and extinction temperatures for the particular reactions that produced the paragenetic sequence. In the models developed in this chapter we consider several examples where the ignition and extinction temperatures are prescribed.

12.2.2. Influence of temperature on fluid pressure.

Changes in temperature influence the fluid pressure in the system. In general the rate of fluid pressure change with time is given by

$$\begin{bmatrix} Rate\ of\ change \\ of\ fluid\ pressure \end{bmatrix} = \begin{bmatrix} [1]\ Rate\ of\ fluid\ pressure\ change \\ arising\ from\ diffusion\ of \\ fluid\ pressure \end{bmatrix} + \begin{bmatrix} [2]\ Rate\ of\ fluid\ pressure\ change \\ arising\ from\ temperature\ change \end{bmatrix}$$
$$+ \begin{bmatrix} [3]\ Rate\ of\ fluid\ pressure\ change \\ arising\ from\ supply\ of\ fluid \\ from\ outside\ the\ system \end{bmatrix} + \begin{bmatrix} [4]\ Rate\ of\ fluid\ pressure\ change \\ arising\ from\ devolatilisation;\ that\ is, \\ fluid\ supply\ from\ within\ the\ system \end{bmatrix}$$

This is a form of reaction-diffusion-advection equation where the diffusion term is [1], the advection term is [3] and the supply terms are [2] and [4]. Hence we expect this expression to behave in many different ways both spatially and temporally depending on competition between diffusion of pressure and generation of pressure. In the early stages of a hydrothermal system reactions that produce fluid are rare so that the term [4] is not important. This is the situation we first explore in the next section. Later in the history of the system this term becomes important and this case is explored as three other models in the next section.

Many mineral reactions also involve large volume changes so that pore pressure changes arise from chemical dilatancy. As an example consider the reaction

3 tremolite + 2 epidote → 3 chlorite + 10 $CaCO_3$ + 21 SiO_2

This reaction results in a volume increase, $\Delta V = +36.7\%$. However if SiO_2 is removed in solution this results in a volume decrease, $\Delta V = -8.7\%$. If $CaCO_3$ is also removed then the total volume decrease is $\Delta V = -42.2\%$. Important questions are: *How are these volume changes expressed in the rock microstructure and what is the influence of such volume changes on fluid pressure and hence on fluid flow and gold solubility*? The answers to these questions are considered in the remainder of this chapter and in Chapter 8.

The influence of temperature on fluid pressure is expressed as (Sulem et al., 2011)

$$\frac{\partial \mathrm{P}^{fluid}}{\partial t} = \kappa^{fluid} \frac{\partial^2 \mathrm{P}^{fluid}}{\partial x_\mathrm{i}^2} + \Lambda \frac{\partial \mathrm{T}}{\partial t} - K \frac{\partial \phi^{plastic}}{\partial t}$$

where κ^{fluid} is the hydraulic diffusivity, $\Lambda = K\phi(\lambda^{fluid} - \lambda^{pore\_volume})$ is the undrained pore fluid thermal expansion coefficient, λ^{fluid} and λ^{pore_volume} are the thermal expansion coefficients of the pore fluid and of the pore volume, ϕ is the porosity and $\phi^{plastic}$ is the porosity induced by plastic deformation, K is the elastic bulk modulus of the dry porous solid and we have assumed the solid matrix is incompressible relative to the compressibility of the fluid.

In a situation with no deformation, $\frac{\partial \phi^{plastic}}{\partial t} = 0$ but if fracturing or brecciation occurs this term becomes important. The pore fluid thermal expansion coefficient, Λ, depends on the rock type, effective stress and temperature (Ghabezloo and Sulem, 2009) and varies between about 0.1 and 0.9 MPa K^{-1}; we assume here a constant value of 0.5 MPa K^{-1}. Thus a 100°C rise in temperature is equivalent to a pore pressure rise of 50 MPa. Such large changes in pore pressure can contribute to the formation of veins and breccias if the pore pressure rise is such that the yield surface is reached.

12.2.3 Equilibrium solubility of gold and quartz.

Finally we want to model the effect of changes in temperature and fluid pressure on the solubility of gold and quartz. We take the data of Loucks and Mavrogenes (1999) and consider the reaction

$$AuHS(H_2S)_3{}^0 + 0.5H_2 \rightarrow Au + 4H_2S$$

This reaction is endothermic with $\Delta_r H^0_{T_0} = 105.353 \pm 2.361$ KJ. A fit (Figure 12.2) to the data of Loucks and Mavrogenes (1999) for the equilibrium solubility of gold, c^{gold} in parts per million by weight, as the complex $AuHS(H_2S)^o_3$ for temperatures between 250°C and 500°C and pressures between 50 MPa and 400 MPa is given by

$$\log c^{gold} = \left[\frac{P^{fluid} + 12.665 \times 10^8}{2.556 \times 10^8} + 5.2769 \right] - \frac{7.572 \times 10^3}{T + 273}$$

where P^{fluid} is in Pascals and T is in degrees Centigrade.

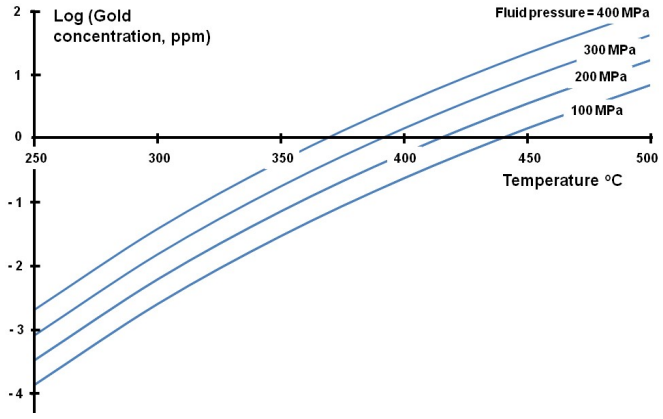


Figure 12.2. Equilibrium solubility of gold as the complex $AuHS(H_2S)^o_3$ in ppm by weight of fluid. Modified from data given by Loucks and Mavrogenes (1999).

If we take the densities of rock and of water as 2700 kg m^{-3} and 1000 kg m^{-3} respectively with a rock porosity of 0.1 then a concentration of 1 gram of gold per tonne of water in the pores of the rock is equivalent to 3.7 $x10^{-2}$ ppm of gold by weight of rock.

For quartz, the equilibrium solubility of H_4SiO_4, $m^{equilibrium}$, with units, $mol_{SiO2}kg_{H2O}^{-1}$, as a function of temperature and fluid pressure is taken from Manning (1994):

$$\log m^{equilibrium} = A + B\log V + C(\log V)^2$$

where $A = -4.66206+0.0034063T +2179.7T^{-1}-1.1292\times 106T^{-2} + 1.3543 \times 1087T^{-3}$, $B = -0.00147180T - 806.97T^{-1}$, $C = 3.9465 \times 10^{-4}T$, V (P^{fluid}, T) ($cm^3\ g^{-1}$) is the specific volume of water and in this case T is the absolute temperature. The specific volume of water over the temperature and fluid pressure ranges of interest is given by Holland and Powell (1991) and we use that approach here following Ord and Henley (1997).

12.3. Model behaviour.

To illustrate the behaviour of the systems depicted in Figure 12.1 we adopt a model 20 km long and 10 km thick with an embedded reaction system 1 km long and 100 m thick (Figure 12.3 top). We consider four situations. The first (equivalent to Figure 12.1 a) involves exothermic alteration reactions where initial silicates are altered to hydrous phases and carbonates as fluid is added to the system; no fluid is produced during these reactions and no deformation occurs. The following three situations (equivalent to Figure 12.1 b) involve deformation of the previously altered system with new reactions that tend to devolatilise the previously formed assemblage so that fluid is produced internally within the system as fluid is simultaneously added to the system. In these models the ambient temperature is higher in the third and fourth examples than in the second. The alteration reactions are endothermic. The permeability of the model is 10^{-16} m^2 with 10^{-15} m^2 for the reaction region; the thermal conductivity is 2.25 $Wm^{-1}K^{-1}$. In model four we decrease the permeability of the country rock to 10^{-20} m^2 and the thermal conductivity of the country rock to 2.0 $Wm^{-1}K^{-1}$. The alteration reactions are assumed to follow the type of kinetics shown in Figure 8.11 (b) and discussed in Section 12.2.1.

12.3.1. Exothermic reactions with no fluid production and no deformation.

For the model situation shown in Figure 12.1 (a) we suppose that the extinction temperature for the reaction is 255°C with an ignition temperature of 300°C. Whilst the reactions are taking place they liberate heat at a rate of 10^{-1} Wm^{-3}. No fluid is produced during the reaction. The initial fluid pore pressure is 3.5 x 10^8 Pa (corresponding to a lithostatic pressure at ≈ 13 km depth) and the initial temperature is 250°C. Other parameters for the model are given in the caption to Figure 12.1.

The types of reactions taking place are represented by reactions such as those below.

$$5\ \text{diopside} + \text{anorthite} + 4\ H_2O + 6\ CO_2 \rightarrow \text{chlorite} + 9\ \text{quartz} + 6\ \text{calcite} \qquad (12.2)$$

$$\Delta H = -783.36\ \text{KJ}$$

$$3\ \text{K-feldspar} + 2\ H^+ \rightarrow \text{muscovite} + 6\ \text{quartz} + 2\ K^+ \qquad (12.3)$$

$$\Delta H = -485.23\ \text{KJ}$$

If we consider reaction (12.2) as an example then 558.7 g of diopside plus anorthite react to produce 783.36 KJ of heat. Assuming a rock density of 2700 kg m^{-3}, this is equivalent to a heat production of 3.79x10^6 Jm^{-3} of rock. Thus the value of 10^{-1} Wm^{-3} assumed in the

modelling is equivalent to the alteration of ≈ 1 cubic metre of rock consisting of diopside and anorthite per 1000 years.

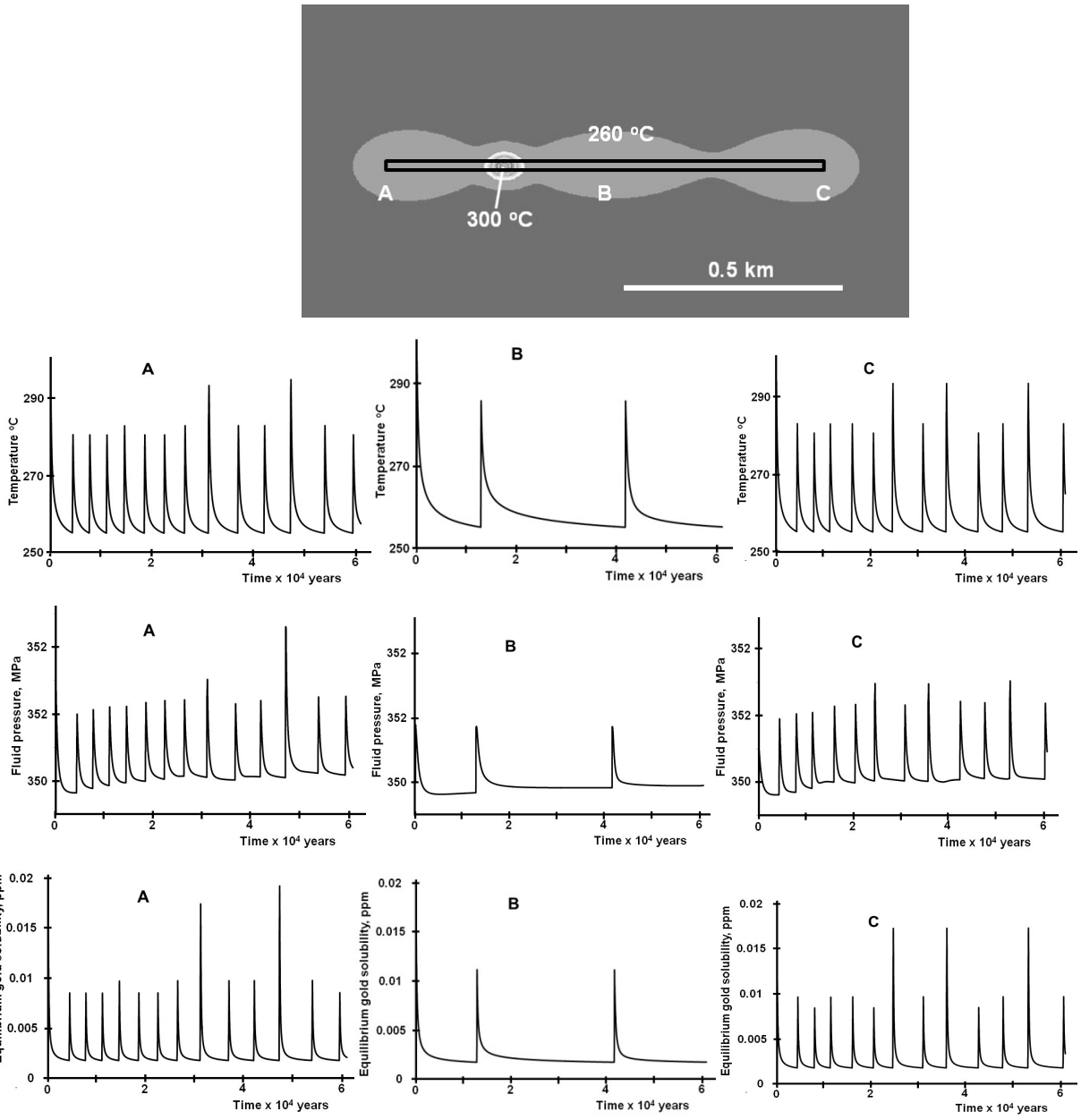


Figure 12.3. Episodic behaviour in a system involving one exothermic reaction and no deformation (Figure 12.1 a) with kinetics given in Figure 8.11 (b). No fluids are released in the reaction and there is no deformation. Top shows the temperature distribution at an instant after 60,000 years. A, B, C are localities where histories are recorded in panels below. First row shows temperature histories at A, B, C. Middle row shows fluid pressure histories at A, B, C. Lower row shows equilibrium gold solubility histories at A, B, C.

Figure 12.3 shows the histories of temperature, fluid pressure and equilibrium gold solubility at three points in the hydrothermal system over a period of 60,000 years. At the ends of the system the oscillations have a period of ≈ 4,500 to 5,000 years whilst in the central regions the oscillations occur every ≈ 30,000 years with a reduced maximum amplitude. The period of thermal fluctuations is governed by the rates at which temperature can rise and fall which are functions of the temperature difference between the system and the country rocks, the thermal conductivity of the country rocks and the temperature distribution in immediately

adjacent elements of the system. The behaviour overall as shown at an instant in the top frame of Figure 12.3 is spatially quite localised. In most regions the temperature sometimes does not reach the ignition temperature before falling again to the extinction temperature. These spatial and temporal characteristics of the temperature behaviour arise from competition between heat production from the exothermic reaction at a site and conduction of heat away or to that site from adjacent sites.

The fluid pressure and equilibrium gold solubility histories mimic the temperature history since they depend only on the temperature. The magnitude of the fluid pressure is a function of competition between thermal expansion of the fluid due to a temperature change and the rate at which fluid pressure can diffuse from the site. Such competitive effects involving diffusion lead to the chaotic spatio-temporal behaviour observed. Although the fluid pressure fluctuations are small they are still sufficient to result in episodic mechanical failure if the stress state is initially close to failure.

The equilibrium gold solubility in this example, although episodic, remains small at $\leq$ 0.02 ppm by weight in the fluid, consistent with the small maximum values of temperature and fluid pressure. These values of gold solubility are less than the value of 0.2 ppm by weight in the fluid proposed by Loucks and Mavrogenes (1999) as a possible maximum for gold solubility carried by an entrance fluid. Hence the fluid in this system is always saturated with gold and each temperature-fluid pressure drop means that gold is deposited as a solid. If the rate constant for gold deposition is much greater than the rate constant for gold dissolution then solid gold will slowly accumulate. At the ends of the system shown in Figure 12.3 the total gold accumulated is $\approx 1.85 \times 10^{-4}$ ppm by weight of rock after 60,000 years or 1.4×10^{-3} ppm after 500,000 years. Thus the grades of gold remain low but localised because of the competitive processes mentioned above and the low maximum values of temperature and fluid pressure. Such a hydrothermal system, although strongly altered, would be classified as a failed mineralising system.

Of importance in understanding paragemetic sequences is that reactions such as (12.2) imply the episodic deposition of chlorite, quartz and calcite synchronous with the deposition of gold. Reactions such as (12.3) imply fluctuatiuons in pH. These fluctuations do not require autocatalytic reactions although such reactions provide another way of generating episodic fluctuations in pH (Henley and Berger, 2000).

12.3.2. Coupling between deformation and endothermic mineral reactions.

Mineralising events (such as deposition of gold) generally overprint the primary alteration assemblages and thus occur later in the history of the system. These mineralising reactions are endothermic and hence enhance the cooling rates of the system. On the other hand, deformation events such as brecciation that are commonly associated with gold deposition are exothermic (Wu et al., 2006). The full coupling between deformation and mineralisation processes has not yet been studied in detail but some relevant results are reported in Alevizos et al. (2014), Veveakis et al. (2014, 2016) and Poulet et al. (2014) with reference to slow earthquakes. Evidently, as the temperature rises during these alteration reactions, endothermic reactions involving devolatilisation of previously formed alteration assemblages and the development of anhydrous silicates such as epidote are initiated by the

higher temperatures and in so doing sap heat produced by deformation from the system. A typical reaction is

$$2\ \text{clinozoisite} + 3\ \text{pyrite} + 2\ \text{calcite} + 3\ \text{quartz} + 5\ H_2O + 1.5\ H_2 \rightarrow 3\ \text{epidote} + 2\ CO_2 + 6\ H_2S \qquad (12.4)$$

This reaction is endothermic with $\Delta H = 5937.5$ KJ. Thus 1649.2 g of solids on the left hand side of the reaction are altered to absorb 5.94×10^6 Joules of heat. This corresponds to 9.74×10^8 J m^{-3} if we take the densities of the solids on the left hand side of the reaction to be 2700 kg m^{-3}. Thus 1 cubic metre of rock reacting in 1000 years represents an absorption rate of 0.03 W.

For the reaction

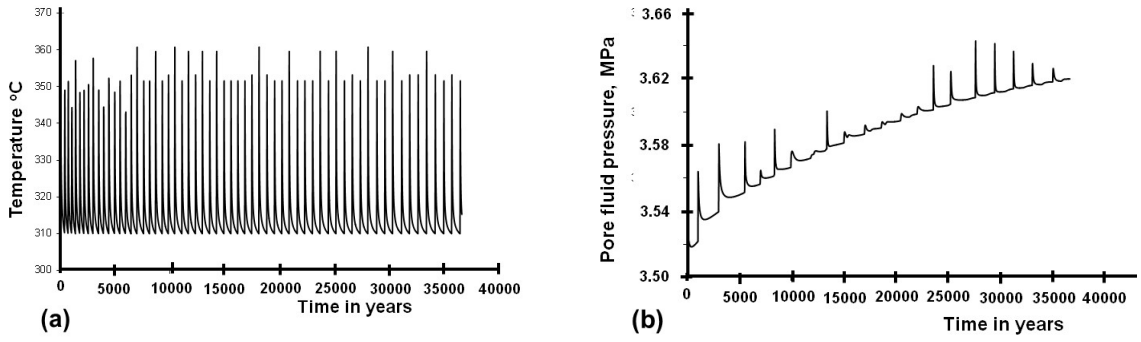
$$6\ \text{actinolite} + 12\ CO_2 + 14\ H_2O \rightarrow 5\ \text{chlorite} + 12\ \text{calcite} + 28\ \text{quartz} \qquad (12.5)$$

$\Delta H = +13409.93$ KJ. Thus 5823 g of solids on the left hand side of the reaction are altered to absorb 13.4×10^6 Joules of heat. This corresponds to 6.22×10^9 J m^{-3} if we take the densities of the solids on the left hand side of the reaction to be 2700 kg m^{-3}. Thus 1 cubic metre of rock reacting in 1000 years represents an absorption rate of 0.197 W.

We now investigate a model with the same geometry as in Figure 12.3 but with an endothermic reaction coupled to heat generated by plastic deformation given by

$$\dot{H}^{deformation} = \beta \sigma_{ij} \dot{\varepsilon}_{ij}$$

where β is the Taylor-Quinney coefficient that measures the amount of heat stored in the material; σ_{ij} is the stress and $\dot{\varepsilon}_{ij}$ is the plastic strain rate. We assume $\beta = 1$ and that the deformation rate is independent of temperature. For a stress of 100 MPa and a strain rate of 10^{-9} s^{-1} the heat generated by plastic deformation is 10^{-1} W m^{-3}. We assume that whilst an endothermic reaction is proceeding, the heat absorption rate for the reaction is 10^{-1} W m^{-3} which corresponds to a reaction such as (12.5) consuming 1 m^3 of rock every 10^3 years. The system also differs from that shown in Figure 12.3 in that fluids are released during the reaction. If we assume that one cubic meter of rock (with density 2700 kg m^{-3}) is altered per year and releases 1% of its weight as water then this is equivalent to 8.5×10^{-10} m^3 of water per second. In the models presented here we assume a release rate of 10^{-10} m^3 s^{-1} which is a slow reaction rate of 1 m^3 of rock, via reactions such as (12.4), every ≈ 10 years. In this model we also show the history of quartz dissolution/precipitation.



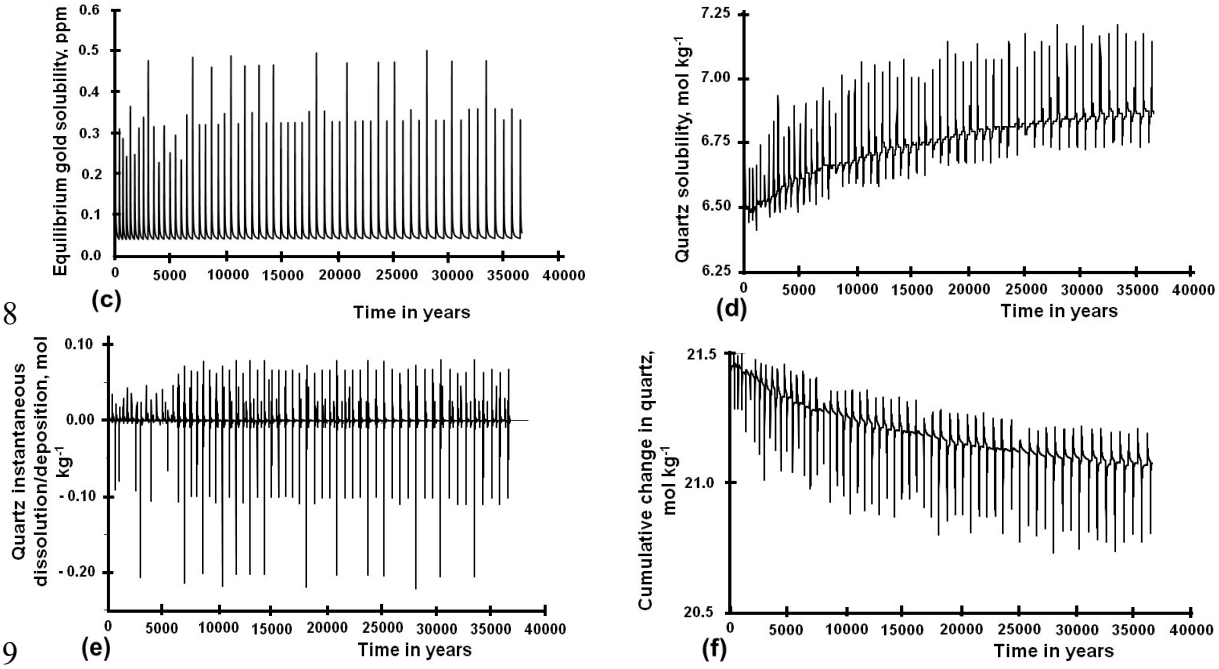


Figure 12.4. Episodic behaviour in a relatively low temperature system involving deformation and one endothermic reaction (Figure 12.1 b) with kinetics given in Figure 8.11 (b). Fluids are released in the reaction. The geometry is as shown in Figure 12.3 top. Each history is at A in Figure 12.3 top over ≈ 37,000 years. (a) Temperature history. (b) Fluid pressure history. (c) Equilibrium gold solubility history. (d) Quartz solubility history. (e) Instantaneous quartz dissolution/deposition history. (f) Cumulative change history of quartz volume.

Figure 12.4 represents the behaviour of a medium temperature orogenic gold deposit where the extinction temperature is 310^{o}C and the ignition temperature, 350^{o}C. The heat absorbed by the reaction is 10^{-1} W m^{-3} and matches that produced by the deformation. Figure 12.4 shows the histories, over a period of ≈ 37,000 years, of temperature, fluid pressure, equilibrium gold solubility and quartz dissolution/precipitation history at the point corresponding to A in Figure 12.3. At this point in the system the temperature oscillations have a period of ≈ 620 years The temperature behaviour overall as shown in Figure 12.5 and at any instant is spatially quite localised; the behaviour resembles that of a flickering flame. These spatial and temporal characteristics of the temperature behaviour arise from competition between heat generated by deformation at a site, the absorption of heat at that site by the endothermic reaction and the conduction of heat away or to that site from adjacent sites; the conduction process is sensitive to the thermal conductivity of the country rock.

The fluid pressure, equilibrium gold solubility and quartz dissolution/precipitation histories mimic the temperature history since they depend only on the temperature although the fluid pressure and gold solubility histories are slightly out of phase with the temperature history; the fluid pressure slowly rises as more fluid is released from the chemical reaction. The magnitude of the fluid pressure is a function of competition between thermal expansion of the fluid due to a temperature change and the rate at which fluid pressure can diffuse from the site; eventually this competition results in a steady fluid pressure. Such competitive effects involving diffusion lead to the chaotic spatio-temporal behaviour observed. Although the fluid pressure fluctuations are small they are still sufficient to result in episodic mechanical failure if the stresss state is initially close to failure.

The equilibrium gold solubility in this example, although episodic, still remains small at ≤ 0.5 ppm by weight in the fluid, consistent with the values of temperature and fluid pressure. These values of gold solubility are more than 0.2 ppm by weight in the fluid proposed by Loucks and Mavrogenes (1999) as a possible maximum for gold solubility carried by an entrance fluid. Hence the fluid in this system is not always saturated with gold but each temperature-fluid pressure drop means that gold is deposited as a solid. If the rate constant for gold deposition is much greater than the rate constant for gold dissolution then solid gold will slowly accumulate. At the position in the system corresponding to Figure 12.4 the total gold accumulated is ≈ 0.4 ppm by weight of rock after 37,000 years. Thus the grades of gold remain low but are localised because of the competitive processes mentioned above. This system would be characterised as a weakly mineralised hydrothermal system.

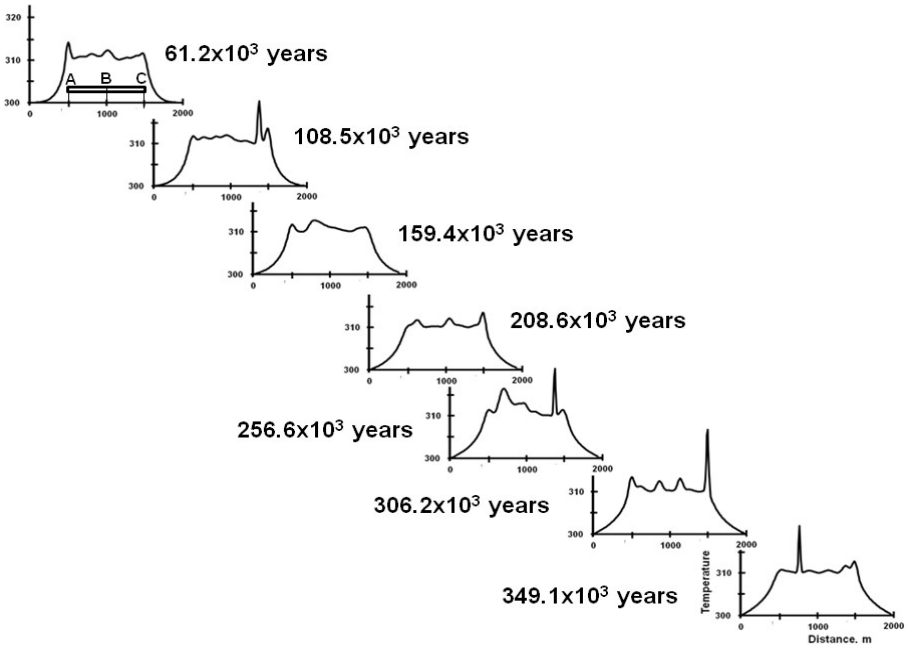
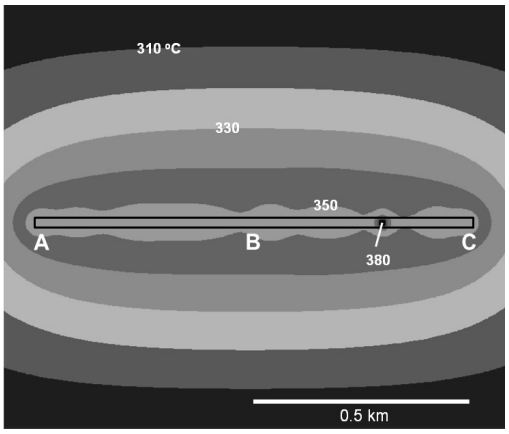


Figure 12.5. Snapshots every 40 to 50,000 years of the temperature distribution in a longitudinal section across the centre of the hydrothermal system of Figure 12.4. The history resembles a flickering elongate combustion system.



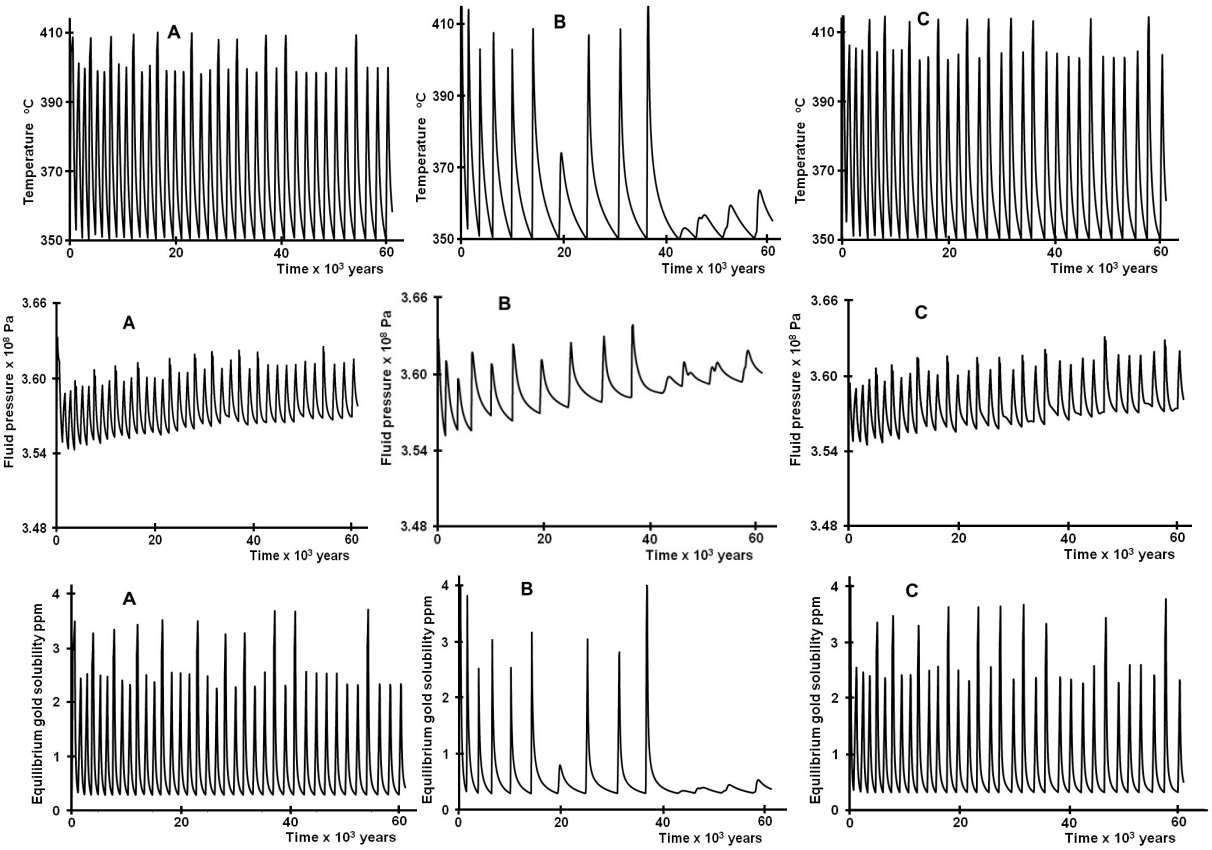


Figure 12.6. Episodic behaviour in a high temperature hydrothermal system with devolatilisation involving one exothermic reaction with kinetics given in Figure 8.11 (b). Fluids are released in the reaction and there is simultaneous continuous deformation. Top shows the temperature distribution at an instant. A, B, C are localities where histories are recorded in panels below. First row shows temperature histories at A, B, C. Middle row shows fluid pressure histories at A, B, C. Lower row shows equilibrium gold solubility histories at A, B, C.

In Figure 12.6 we present a high temperature system where the extinction temperature is 350^{o}C and the ignition temperature, 410^{o}C. The heat absorbed by the reaction is 10^{-1} W m^{-3} and matches that produced by the deformation. Figure 12.6 shows the histories of temperature, fluid pressure and equilibrium gold solubility at three points in the hydrothermal system over a period of 60,000 years. In most parts of the system the oscillations have a period of ≈ 1,600 to 1,900 years whilst in the central regions the oscillations occur every ≈ 4,600 years with a reduced maximum amplitude. The behaviour overall as shown at an instant in the top frame of Figure 12.6 is spatially quite localised. In the end regions the temperature sometimes does not reach the extinction temperature before falling again to the ignition temperature. These spatial and temporal characteristics of the temperature behaviour arise from competition between heat production from the exothermic reaction at a site and conduction of heat away or to that site from adjacent sites.

The fluid pressure and equilibrium gold solubility histories mimic the temperature history since they depend only on the temperature although the fluid pressure and gold solubility histories are out of phase with the temperature history since fluid is not released from the devolatilising reaction until after the peak temperaure. The magnitude of the fluid pressure is a function of competition between thermal expansion of the fluid due to a temperature change and the rate at which fluid pressure can diffuse from the site. Such competitive effects involving diffusion lead to the chaotic spatio-temporal behaviour observed. Although the fluid

pressure fluctuations are small they are still sufficient to result in episodic mechanical failure if the stress state is initially close to failure.

The equilibrium gold solubility in this example, although episodic, reaches ≈ 3.5 ppm by weight in the fluid, consistent with the relatively high values of temperature and fluid pressure. These values of gold solubility are greater than 0.2 ppm by weight in the fluid proposed by Loucks and Mavrogenes (1999) as a possible maximum for gold solubility carried by an entrance fluid. Hence the fluid in this sytem is always under-saturated with gold and each temperature-fluid pressure drop means that gold is deposited as a solid only in amounts governed by the concentration of gold in solution. If the rate constant for gold deposition is much greater than the rate constant for gold dissolution then solid gold will slowly accumulate. At the ends of the system shown in Figure 12.6 the total gold accumulated is ≈ 7.5 ppm by weight of fluid in the rock or ≈ 0.3 ppm by weight of rock after 60,000 years or 2.5 ppm by weight of rock after 500,000 years. Thus the grades of gold can be significant but again are localised because of the competitive processes mentioned above. We discuss a quantitative model for gold deposition in the Discussion. The coupling between temperature, fluid pressure and equilibrium gold solubility is shown in Figure 12.7.

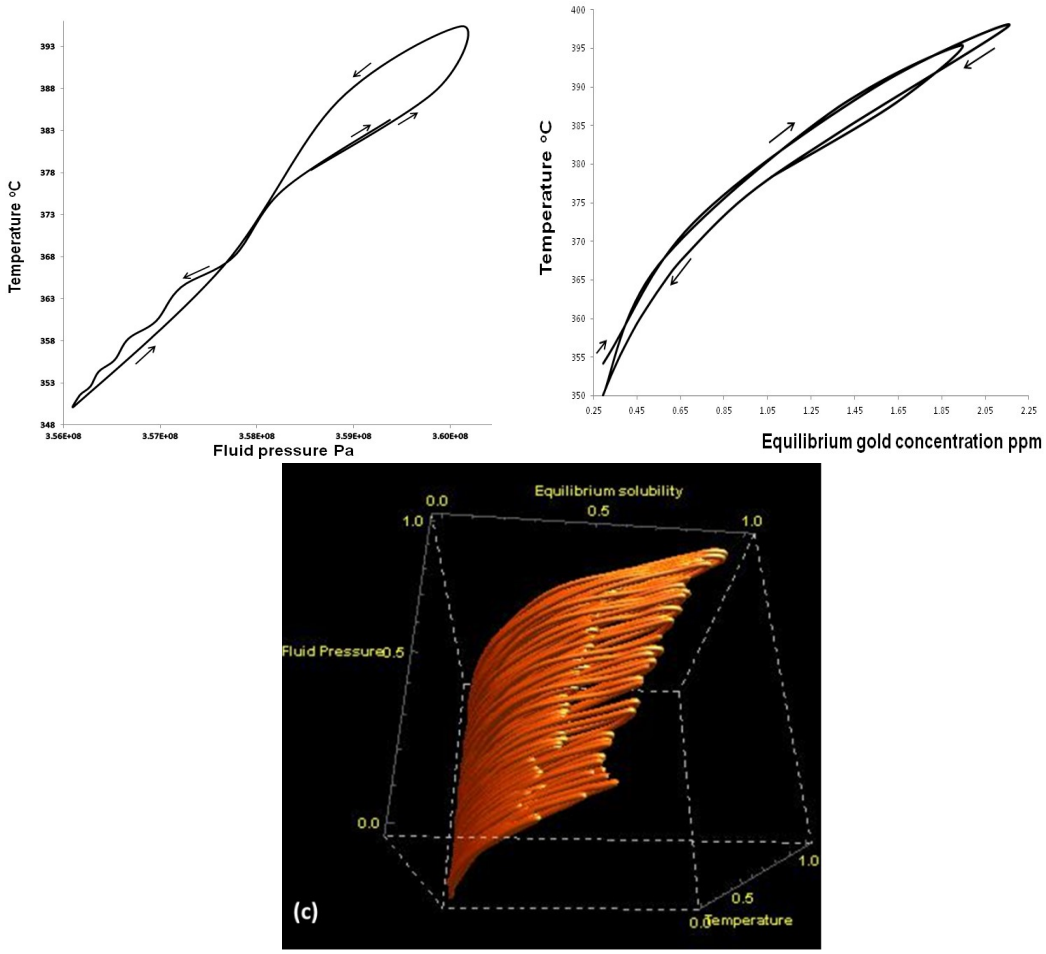


Figure 12.7. Phase plots in temperature-fluid pressure – equilibrium gold solubility space. (a) A section in the temperature-fluid pressure plane. (b) A section in the temperature – equilibrium gold solubility plane. (c) The three dimensional phase plot with axes normalised to maximum values of temperature, equilibrium gold solubility and fluid pressure.

In Figure 12.8 we show a relatively high temperaure situation with a devolatilising endothermic reaction coupled to deformation. The parameters are the same as in Figure 12.6 except that the permeability of the country rock is decreased to 10^{-20} m^2 and the thermal conductivity decreased to 2 W m^{-1} K^{-1}. The result is an increased pore pressure since fluid pressure cannot leak easily from the system and an increase in the frequency of temperature oscillations since the system can heat up faster. The steady increase in pore pressure results in a steady increase in the equlibrium solubilty of gold (Figure 12.8 c).

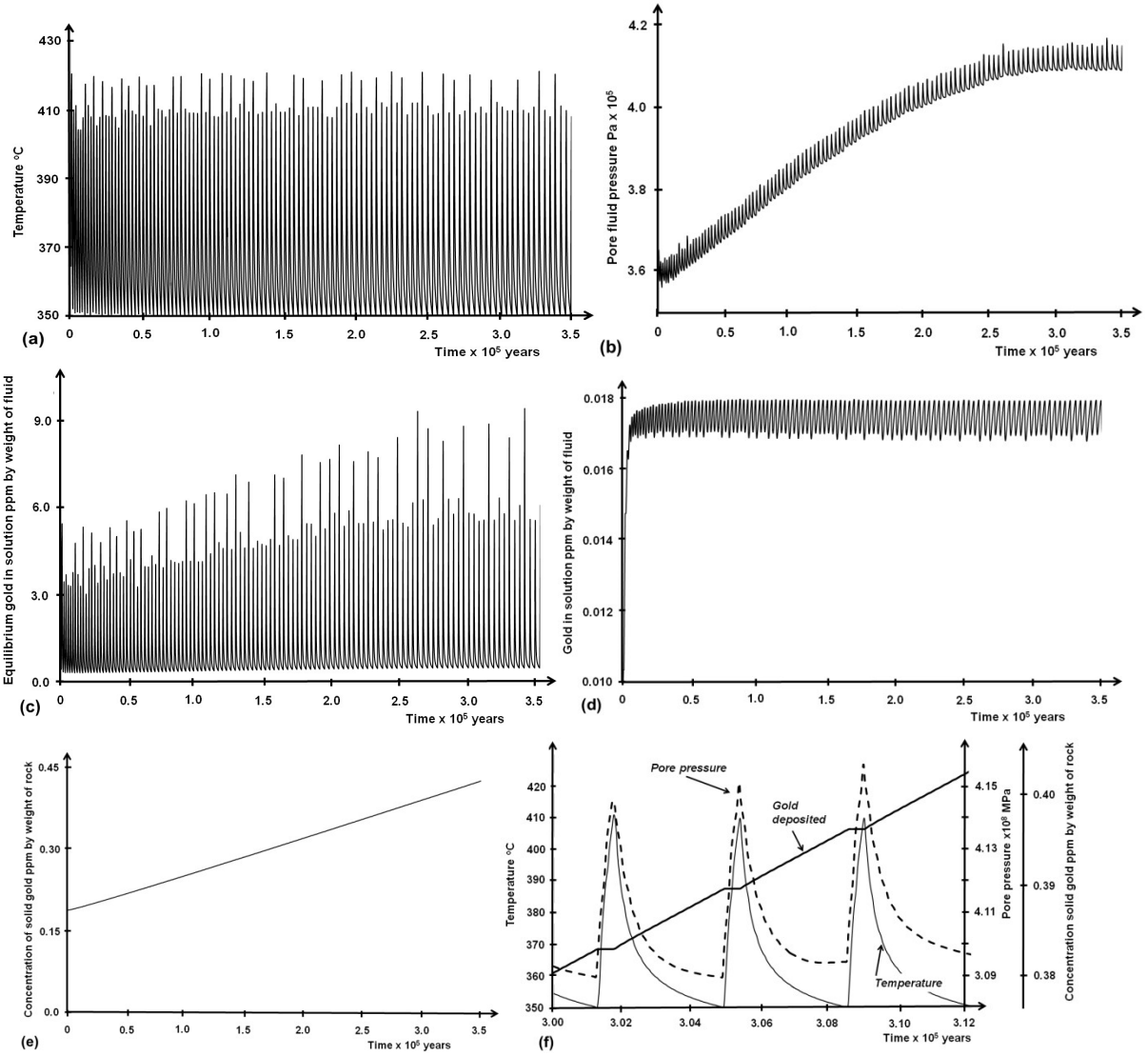


Figure 12.8. Episodic behaviour in a high temperature hydrothermal system with devolatilisation involving one exothermic reaction with kinetics given in Figure 8.11 (b). The net input of gold is 10^{-12} ppm s^{-1} m^{-2}. Fluids are released in the reaction and there is simultaneous continuous deformation. The permeability of the country rock has been decreased, relative to Figure 12.6, to 10^{-20} m^2 and the thermal conductivity of the country rock is decreased to 2.0 W m^{-1} K^{-1} relative to Figure 12.6. Histories are at the equivalent position A in Figure 12.6. (a) History of temperature; oscillation period is ≈ 3000 years. (b) History of fluid pressure. (c) History of equilibrium gold solubility. (d) History of gold concentration in solution in ppm per weight of fluid as calculated from (12.9) and (12.10) in the Discussion. (e) History of deposited gold concentration in ppm per weight of rock as calculated from (12.11) and (12.12) in the Discussion. (f) Summary showing detail, over a period of 12,000 years, of relations between temperature, fluid pressure and solid gold deposited; all oscillations are in phase.

12.4. Discussion.

12.4.1. Summary.

Here we summarise the results of this chapter before proceeding to a quantitative model of gold deposition. In the early parts of the evolution of orogenic gold systems most mineral reactions are exothermic and mineral reaction rates are dominated by the supply of fluids to the reaction sites. The exothermic nature of the reactions together with the exponential dependence of reaction rate on temperature and the linear dependence of reaction rate on nutrient supply mean that reaction rates oscillate as the reaction rate competes with the rate of supply of heat and of nutrients in incoming fluids. We have considered relatively simple behaviour of the exothermic reaction, $A \rightarrow B$, but even more complex behaviour occurs if nonlinear rates of heat supply/removal are taken into account (Chapter 8; Gray and Scott, 1990, Chapter 7). The important point is that the reaction rate is highly sensitive to the local fluid flow rate and so highly reacted parts of the rock mass can exist immediately adjacent to unreacted parts simply because of differences in permeability and/or plastic-chemical dilatancy.

The outcome of competition between fluid supply and temperature dependent reaction rates is episodic fluctuations in temperature as the reaction cycles through ignition → extinction → ignition phases as illustrated in examples in Chapter 8. These temperature fluctuations produce fluctuations in fluid pressure which, in the absence of inelastic dilation, have amplitudes governed by the rate at which fluid pressure can diffuse away from the reaction site and on the thermal pressurisation coefficient, Λ, which lies in the range 0.1 to 0.9 MPa /C^{o} and hence has an important effect. Such pressure fluctuations can initiate fracturing and brecciation if the pore fluid is already close to being pressured lithostatically.

The important additional feature resulting from the fluctuations in pressure and temperature is the episodic influence on the equilibrium solubility of gold and of other important constituents of orogenic gold deposits, quartz and carbonates. Thus, assuming the reaction $AuHS(H_2S)_3^{\ 0} + 0.5H_2 \rightarrow Au + 4H_2S$ and the results depicted in Figure 12.2 the system oscillates with respect to the equilibrium solubility of gold as shown in Figures 12.3, 12.4, 12.6 and 12.8. Many authors including Loucks and Mavrogenes (1999) and Henley and Berger (2000) have pointed to the difficulty in reaching the high equilibrium solubilities indicated in Figure 12.2 and modelled in Figures 12.3, 12.4, 12.6 and 12.8. Loucks and Mavrogenes (1999) indicate that 0.2 ppm by weight of gold in solution is near a maximum one could expect to see in any inlet feed supply to a gold system. In this chapter we mainly assume an input gold concentration of 10 ppb by weight of fluid. Hence there is a problem in developing the high bonanza grades (ounces per tonne of rock) that are seen in some gold deposits.

For the low temperature situation shown in Figure 12.3 we see about 13 oscillations in temperature and fluid pressure in a period of 60,000 years. The results for the equilibrium solubility of gold in this system show that the fluids in the system are saturated with gold for all of the history of alteration so that gold is deposited every time the pressure and temperature drop. In such a system gold concentrations of $\approx 10^{-2}$ ppm by weight of rock is an upper limit to the grades that could develop if the system lasts 500,000 years. Thus the deposit although strongly altered is very weakly mineralised.

For the medium temperature situation shown in Figure 12.4 there are about 60 oscillations in temperature and fluid pressure in a period of ≈ 36,000 years. The concentration of gold in solution exceeds that we could expect as the equilibrium solubility in any incoming stream so the system is under-saturated with respect to gold until the equilibrium solubility reaches low values. We expect a deposit of disseminated, interesting grades of gold, reaching perhaps 1-2 grams per tonne.

For the higher temperature situation shown in Figure 12.6 we see about 37 oscillations in temperature and pressure over 60,000 years with equilibrium concentrations of gold oscillating between ≈ 0.2 and ≈ 4 ppm by weight in the fluid. The issue now in this high temperature situation is whether the concentration of gold in solution can rise above say 0.2 ppm by weight or is it fixed at the inlet concentration of $\ll$ 0.2 ppm throughout each cycle? If the fluid remains under-saturated throughout its history with a concentration of 0.2 ppm by weight of fluid then the grade of the deposit at end locations will be ≈ 0.3 ppm by weight of rock if the system lasts for 60,000 years or ≈ 3.3 ppm by weight of rock if the system lasts for 10^6 years. These relatively low grades suggest that gold enhancement process may operate in some systems to increase the gold concentration in solution towards equilibrium values as the system evolves. Below we present a model that enables such enhancement as the system evolves through a process that involves deposition of gold as the temperature and pressure drops in a particular cycle and relatively minor dissolution of deposited gold as the temperature and pressure rise in the next cycle. We then consider localisation behaviours that can lead to bonanza grades of gold.

12.4.2. A model for progressive enrichment of gold in solution.

We consider the reaction

$$\mathrm{Au} + 4\mathrm{H_2S} \underset{k_-}{\overset{k_+}{\rightleftharpoons}} \mathrm{AuHS}\left(\mathrm{H_2S}\right)_3^{\,0} + 0.5\mathrm{H_2} \qquad (12.6)$$

where k_+ and k_- are the rate constants for the dissolution and deposition reactions respectively. Since the reaction proceeding to the right is endothermic we expect from transition state theory, that the temperature dependence of the rate constant for deposition of gold, $k_{deposition}$, is greater than that for the rate constant for dissolution, $k_{dissolution}$ (Schott et al., 2009). Both the dissolution and deposition processes are heterogeneous and so both the rates of deposition and of dissolution of gold depend on the concentration of gold in solution and the amount of gold precipitated. By analogy with processes that operate in fixed bed chemical reactors (Aris, 1975) the precise mechanisms of gold deposition and dissolution and their dependencies on solid gold concentration are likely to be quite complicated but we assume simple linear dependencies for the want of better models. In the limited modelling we have so far considered the precise mechanism makes little difference to the qualitative behaviour of the system. In addition, gold is added to the system in solution at a constant rate. In what follows we consider gold dissolution and deposition processes as the temperature and pore pressure rise and fall as in the histories depicted in Figures 12.6 and 12.8.

Change in gold concentration during a temperature/fluid pressure increase.

We assume a system in which the reaction (12.6) occurs. The problem we want to consider involves episodic changes in temperature and fluid pressure so that the equilibrium solubility of gold fluctuates in time as do the rate constants, through an Arrhenius

dependence, as the temperature changes. These changes also produce episodic fluctuations in the activities of H_2 and of H_2S. Since the forward and reverse reactions are heterogeneous the rates of the reactions also depend on the current surface area of solid gold. The problem of tracking the deposition of gold is therefore quite complex with different behaviours depending on the evolving variables, temperature, pore pressure, equilibrium gold solubility, the activities of gaseous phases and the gold surface area. Instead of exploring the complete parameter space involving these variables, we explore a subsection of parameter space and adopt a simple approach to the problem in which the fluctuations in rate constants, equilibrium gold solubility and surface area can be explored.

We begin by writing the rates of gold dissolution and deposition in the following ways:

$$\frac{dx}{dt} = \delta + k_+^{/} x\left(1 - \frac{x}{x^*}\right) y \qquad (12.7)$$

$$\begin{bmatrix} Rate\ of\ change \\ of\ gold\ in \\ solution \end{bmatrix} = \begin{bmatrix} Net\ rate\ of \\ addition\ of \\ gold\ in \\ solution \end{bmatrix} + \begin{bmatrix} Rate\ of\ dissolution\ of \\ gold\ modified\ by\ a \\ saturation\ term \end{bmatrix}$$

$$\frac{dy}{dt} = -k_-^{/} xy \qquad (12.8)$$

$$\begin{bmatrix} Rate\ of\ change \\ of\ solid\ gold \end{bmatrix} = -\begin{bmatrix} Rate\ of\ solution\ of \\ gold \end{bmatrix}$$

In these equations x and y are the concentrations of gold in solution and of solid gold, t is time, $k_+^{/}, k_-^{/}$ are the forward and reverse rate constants expressed as functions of the activities of H_2S and of H^2, that is, $k_+^{/} = k_+ a_{H_2S}^4$ and $k_-^{/} = k_- a_{H_2}^{1/2}$. Both these rate constants follow an Arrhenius relation: $k = k^0 \exp(-E_a / RT)$. x^* is the current equilibrium solubility of gold, δ is the net flux of gold in solution into the system and the term $\left(1 - \frac{x}{x^*}\right)$ expresses the slowing of the dissolution rate as the equilibrium solubility is approached so that the dissolution rate is zero when $x = x^*$. The dissolution rate of gold also slows as y → 0. (12.7) is a form of logistic equation which has been well explored; Banks (1994) discusses the behaviour of this equation for situations where δ, the k's and x* are functions of time.

In all the following models we assume the following values for parameters: $k^{0/}_+ = 1.97\text{x}10^{-3}$ mol s^{-1}, $k^{0/}_- = 1.97\text{x}10^{-1}$ mol s^{-1}, $E_{a+} = 1.1\text{x}10^5$ J mol^{-1}; $E_{a-} = 1.0\text{x}10^4$ J mol^{-1}. We have explored wide variations in these parameters and the behaviour of the system seems insensitive to the values selected.

Although it is unlikely that the concentration of gold in solution ever reaches the higher values of equilibrium gold solubility, x^*, shown in Figures 12.6 and 12.8, x^* is still an important parameter since it has an instantaneous influemce on the rate of dissolution through (12.7). At low values of x^*, dissolution is inhibited or prevented, whereas at high values of x^*, dissolution is enhanced.

Change in gold concentration during a temperature/fluid pressure decrease.

For that part of a cycle where there is a decrease in temperature and fluid pressure we write for the rates of change of gold in solution and for gold deposited logistic equations of the forms (12.9) and (12.10).

$$\frac{dx}{dt} = \delta - k'_{-}x\left(1 - \frac{x}{x^*}\right)$$

$$\begin{bmatrix} Rate\ of\ change \\ of\ gold\ in \\ solution \end{bmatrix} = \begin{bmatrix} Net\ rate\ of \\ addition\ of \\ gold\ in \\ solution \end{bmatrix} - \begin{bmatrix} Rate\ of \\ deposition\ of \\ solid\ gold \end{bmatrix} \qquad (12.9)$$

$$\frac{dy}{dt} = k'_{-}x\left(1 - \frac{x}{x^*}\right)$$

$$\begin{bmatrix} Rate\ of\ change \\ of\ gold\ being\ deposited \end{bmatrix} = \begin{bmatrix} Rate\ of \\ deposition\ of \\ gold\ as\ solid \end{bmatrix} - \begin{bmatrix} Rate\ of \\ solution\ of \\ solid\ gold \end{bmatrix}$$

(12.10)

For the temperature-fluid pressure decrease part of the cycle we first explore the equations as written in (12.9) and (12.10) and then explore a situation where the deposition rates depend on the concentration of solid gold as in (12.11) and (12.12).

$$\frac{dx}{dt} = \delta - k'_{-}x(1-y)y \qquad (12.11)$$

$$\frac{dy}{dt} = k'_{-}x(1-y)y \qquad (12.12)$$

The behaviour of gold dissolution and deposition is shown for three situations in Figures 12.9, 12.10 and 12.11 for the high temperature model of Figure 12.6. Figure 12.9 shows the effect of decreasing the thermal conductivity and permeability of the country rocks starting from an initial solid gold concentration of 0.185 ppm by weight of rock. The efficiency of the gold deposition process is 68% which represents an increase of 57% over situations where the thermal conductivity of the country rocks is 2.25 W m^{-1} K^{-1}. Figures 12.10 and 12.11 highlight the differences in grade resulting from net input flows of 10^{-12} and 10^{-10} ppm m^{-2} s^{-1}. The wall rock thermal conductivity is 2.25 W m^{-1} K^{-1}.

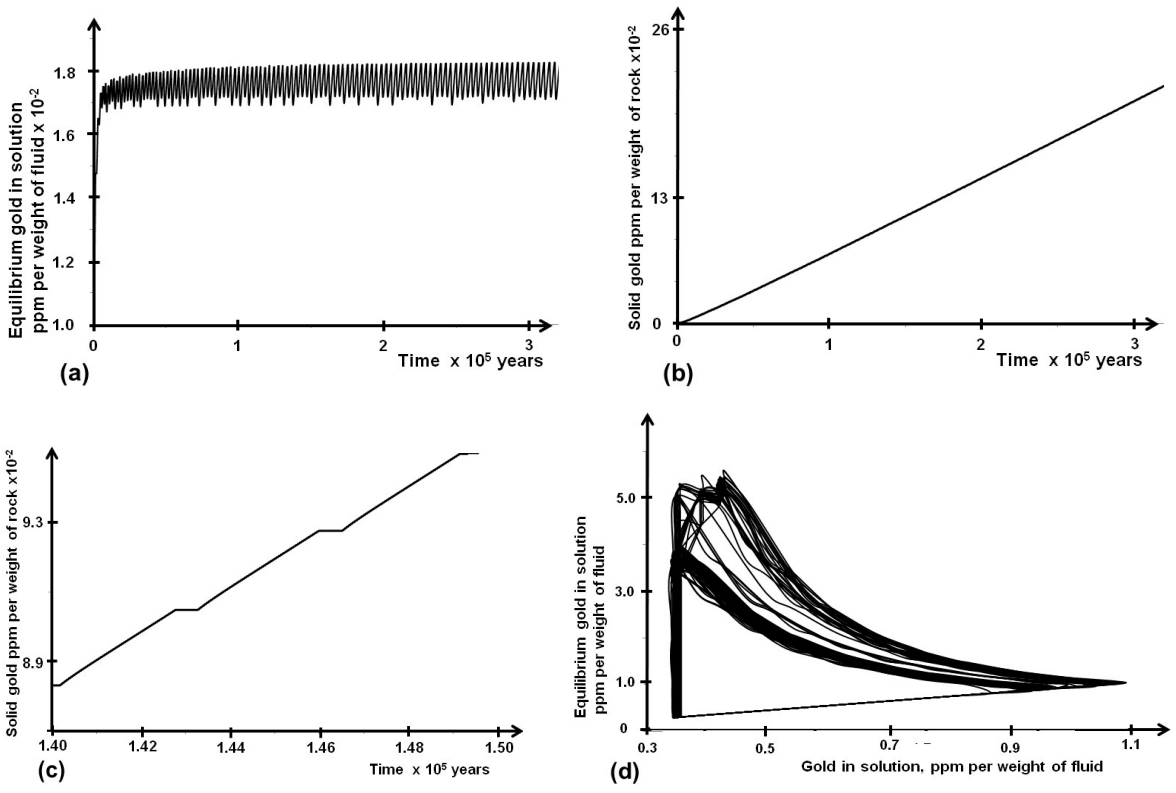


Figure 12.9. Solutions to (12.7) and (12.8) for $\delta = 10^{-12}$ ppm m^{-2} s^{-1}, $x_0 = 10^{-2}$ ppm and $y_0 = 10^{-2}$ ppm. Other parameters are given in the text. Model is the same as Figure 12.6. (a) Concentration of gold in solution in ppm by weight of fluid. (b) Concentration of solid gold in ppm per weight of rock. (c) Detail of (b) showing periods of deposition oscillating with periods of negligible dissolution or deposition. (d) The attractor in phase space: equilibrium solubility of gold – concentration of gold in solution.

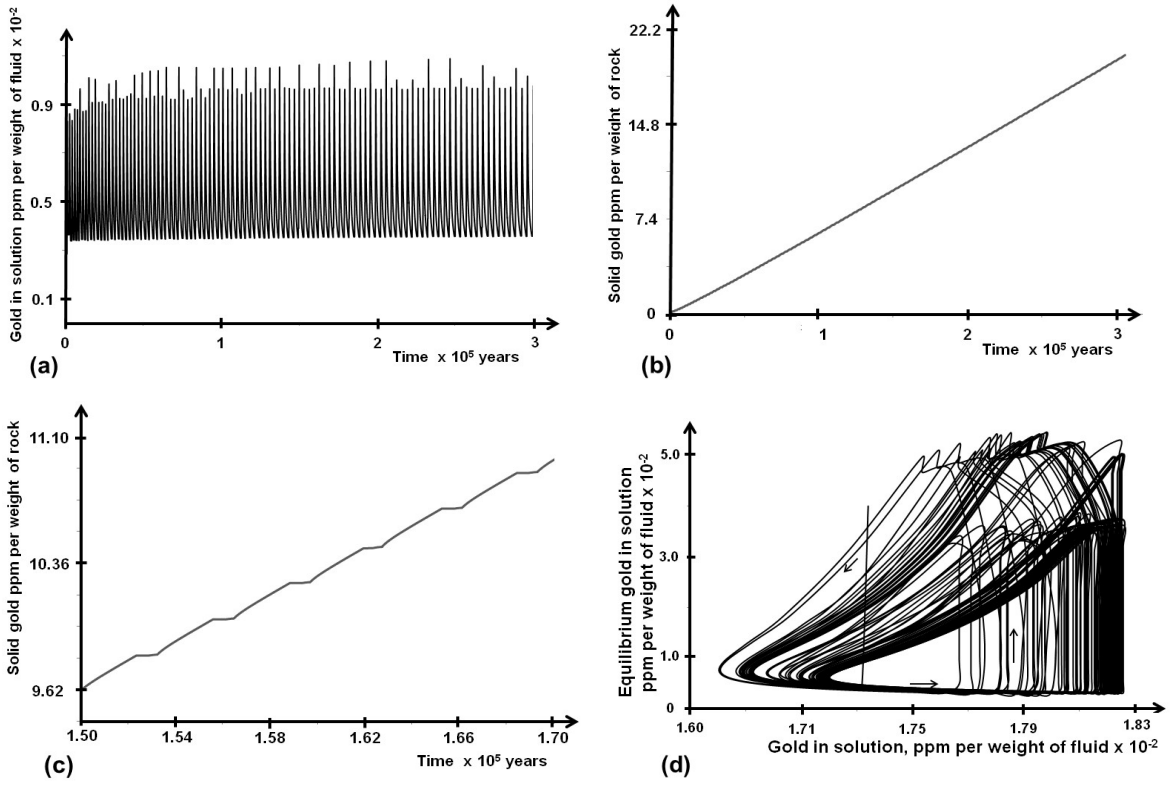


Figure 12.10. Solutions to (12.9) and (12.10) for $\delta = 10^{-10}$ ppm m^{-2} s^{-1}, $x_0 = 10^{-2}$ ppm and $y_0 = 10^{-2}$ ppm. Other parameters are given in the text. Model is the same as Figure 12.6. (a) Concentration of gold in solution in ppm by weight of fluid. (b) Concentration of solid gold in ppm per weight of rock. (c) Detail of (b) showing periods of deposition oscillating with periods of negligible dissolution or deposition. (d) The attractor in phase space: (equilibrium solubility of gold – concentration of gold in solution).

In Figure 12.11 we show some of the results for a more complicated gold deposition process given by (12.11) and (12.12). The gold dissolution process is now out of phase with respect to the equilibrium concentration of gold in solution (Figure 12.11 a) but this makes little difference to the overall gold grade (Figure 12.11 b). Since the equilibrium gold concentration in solution is in phase (not shown) with the pore presssure this means that gold deposition is not coincident with brecciation or fracturing events that occur as the effective stress reaches the yield stress.

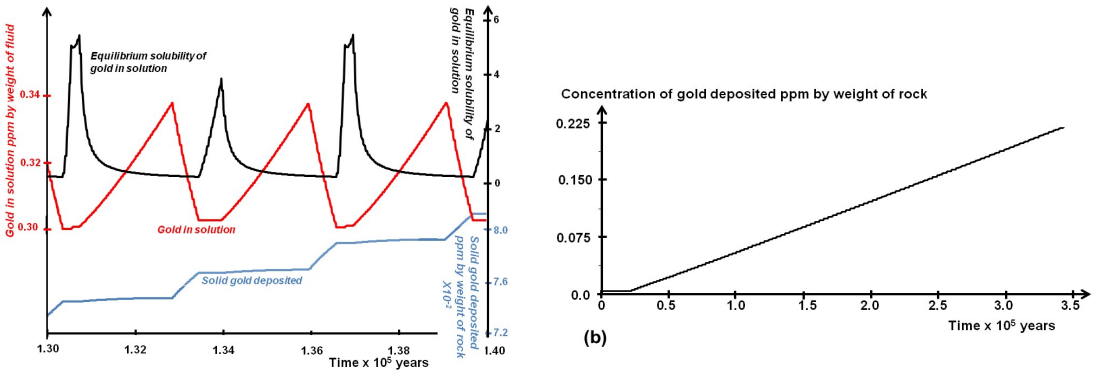


Figure 12.11. Solutions, over a time period of 10,000 years, to (12.11) and (12.12) for $\delta = 10^{-12}$ ppm m^{-2} s^{-1}, $x_0 = 10^{-2}$ ppm and $y_0 = 10^{-2}$ ppm. Other parameters are given in the text. Otherwise the model is the same as Figure 12.6. (a) Summary of coupling between equilibrium gold in solution, gold in solution and solid gold deposited. (b) History of solid gold deposited in ppm by weight of rock over 350,000 years.

12.5. Parameter space.

In this chapter we have explored a very restricted part of the parameter space that describes the various behaviours of a highly nonlinear system. The aim has been to select a simple subset of the system in which the basic principles of nonlinear behaviour can be demonstrated. As we indicated earlier some of the dimensionless parameters that describe behaviour in this subset are:

- The Damköhler number, *Da*, is a measure of the importance of the time scale of fluid flow relative to that for chemical reaction. In the system we examined changes in *Da* result in simple oscillatory behaviour of the chemical reaction. In many systems (Gray and Scott, 1990) the control of *Da* on the chemical reaction rate is much more complicated.
- The Newtonian cooling time measures the importance of the thermal cooling time scale relative to the chemical time scale. This is also important in controlling chemical reaction rates (Aris, 1999). It is influenced strongly by the shape of the system and by the thermal conductivity of the wall rocks and so is important in studies of specific orogenic gold systems; we expect systems of different shapes to behave in different manners as discussed below. The limited exploration we have done indicates that systems with a wall

rock thermal conductivity of 1.8 W m^{-1} K^{-1} have gold grades 17% higher that if the wall rock thermal conductivity is 4 W m^{-1} K^{-1}.

- The Arrhenius number, *Ar*, measures the importance of the thermal energy relative to the activation energy for chemical reactions and for rate sensitive deformation processes. *Ar* defines the spectrum of chemical reactions that occur in a particular system (Law, 2006, pp 60-62) and hence is fundamental in defining the paragenetic sequence we see in a particular system. *Ar* is also fundamental in defining the deformation behaviour of the system (Veveakis et al., 2010).

In addition, two other dimensionless numbers need to be included in any extension of what has been done here:

- The Gruntfest number, *Gr*, measures the importance of the heat generated by deformation to that absorbed or generated by chemical reactions. *Gr* is important in defining the magnitude of the temperature increase possible for coupled deformation/chemical reactions and hence influences the deformation rate in systems where rate dependent constitutive behaviour is included (Veveakis et al., 2010, 2014; Alevizos et al., 2014; Poulet et al., 2014).
- The Lewis number, *Le*, is a measure of the importance of heat transport by diffusion to mass transport. *Le* is important in defining the magnitude of the pore pressure increase possible for a particular temperature increase as fluid diffuses from the site of the temperature increase (Veveakis et al., 2014; Alevizos et al., 2014; Poulet et al., 2014). In the systems explored here the wall rocks for the system are relatively permeable and hence pore pressure leaks away as devolatilisation proceeds and the temperature increases. If the wall rocks are relatively impermeable, as would be the case for instance if the system is embedded in black shales, the Lewis number is smaller and the pore pressure increases would be larger.

Future work needs to concentrate on exploration of what are envisaged to be important parts of this five-fold parameter space. For some systems parts of this space will be more relevant than others.

12.6. The influence of geometry.

Since the chemical reaction rates in an open flow thermodynamic system are highly sensitive to the supply of heat to the system and the oscillatory behaviour is sensitive to the rate at which heat can be lost from the system, the cooling regime becomes an important parameter in controlling the behaviour of the system. An important element in this control is the ratio of the surface area of the reacting system to its volume. To illustrate this effect in Figure 12.12 we show the behaviour of a system very similar to that modelled in Figures 12.3, 12.4, 12.6 and 12.8 but with an offset, and hence a thickening, of the system in the central region. This change in geometry results in changes in the heat diffusing from the central region to the country rock and in heat diffusing from adjacent areas of the reacting system. The thermal behaviour in this central region is now quite different to that in Figures 12.3, 12.4, 12.6 and 12.8 with more oscillations in temperature and larger amplitudes of

fluctuations in the thickened region. Thus we expect the system shown in Figure 12.12 to produce higher grades of gold than in the thinner geometries.

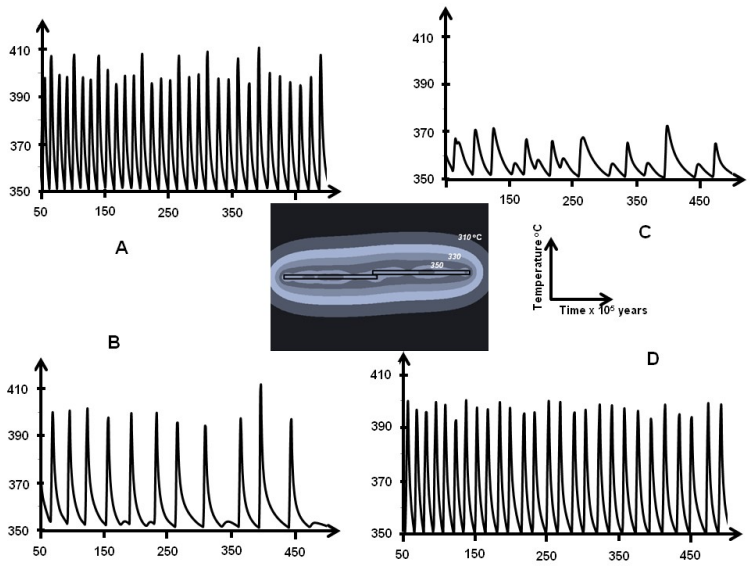


Figure 12.12. Episodic behaviour in a system involving one exothermic reaction with kinetics given in Figure 8.11 (b). No fluids are released in the reaction and there is no deformation. Middle panel shows the temperature distribution at an instant. A, B, C, D are localites where histories are recorded in panels below. Remaining panels shows temperature histories at A, B, C and D.

12.7. What controls the grade of an orogenic gold deposit?

The maximum gold grade, $g^{maximum}$, possible in a deposit is the integrated flux of gold into the system over the lifetime, $t^{lifetime}$, of the deposit:

$$g^{maximum} = \int_0^{t^{lifetime}} \delta dt$$

In the absence of any processes that localise gold deposition this grade will be uniformly distributed in the system. With δ=2.7 x 10^{-12} ppm by weight of fluid m^{-2} s^{-1} over 500,000 years, $g^{maximum}$ = 1.58 ppm by weight of rock. This corresponds to a fluid flux through a system with a lithostatic pore pressure gradient, a permeability of 10^{-17} m^2, a fluid viscosity of 10^{-4} Pa s, an input gold concentration in solution of 1 ppb by weight of fluid and perhaps losses in the outflow of 0.1 ppb by weight of fluid. Any change in these values will change the result proportionally but these values seem reasonable and conservative. If for instance the permeability was increased to 10^{-16} m^2 then the maximum grade is 15.8 ppm by weight of rock. Thus it seems possible but difficult to reach bonanza grades of many ounces per tonne (1 ounce troy $tonne^{-1}$ = 31.1 g $tonne^{-1}$). Even a grade of 1ppm per weight of rock requires a mechanism to deposit the gold from solution and we are proposing that aseismic intrinsic oscillations in temperature as described here are one way of achieving this. High bonanza grades require some process for localisation of gold deposition within the system and we discuss such processes later in the Discussion. In the models presented here the system always loses gold in solution as the mineralising process proceeds. In general the efficiency, measured by the ratio of amount of gold deposited in the system to the amount of gold added to the system, is ≈ 57%. In Figure 11 (e) where the thermal conductivity of the country rock has been reduced to 2 W m^{-1} K^{-1} the efficiency rises to ≈ 68 %.

709 The critical factors required to optimise gold grades in a system with episodic
710 behaviour are processes that maximise the temperature and pore fluid pressure so that the
711 equilibrium solubility of gold is maximised (see Figure 12.2). The temperature is controlled
712 by the ΔH of mineral reactions that occur at the time of gold deposition together with heat
713 liberated by deformation. Strongly exothermic reactions and fast deformation rates lead to
714 higher frequency temperature oscillations than for situations with endothermic reactions and
715 no deformation. Temperatures are higher if the country rocks have low thermal conductivity
716 typical of shales or pelites in general. Fluid pressure depends on three factors: The
717 temperature, concurrent release of fluids from devolatilising reactions and the permeability of
718 the country rocks; low permeability rocks such as pelites, quartzites and mafic rocks inhibit
719 the leakage of fluid pressure from the system and hence result in higher fluid pressures. All of
720 these factors are recorded in the paragenetic sequence and in the relation of this sequence to
721 the deformation history. The key to understanding orogenic gold systems is to view them in
722 terms of the energy balance between chemical, hydrological, thermal and deformation
723 processes that are observed in the system.
724 The early stage of alteration in a system where exothermic reactions dominate and
725 fluids such as CO_2 and H_2O are consumed to produce carbonates and hydrous silicates, in a
726 sense, serves to set the system up for a later mineralisation stage. This early stage increases
727 the temperature of the system so that reactions with larger activation energies can ignite and
728 provides a readily available source of stored CO_2 and H_2O in mineral crystal structures for
729 access at a later stage. The low temperatures and the consumption of fluids, both of which
730 contribute to low fluid pressures, mean that the equilibrium solubility of gold is small and
731 mineralisation, if present, is of low grade.
732 The later stages of system evolution involve higher temperatures and the release of
733 fluids. Hence higher fluid pressures develop if the permeability structure of the system allows
734 this to happen. Such an environment may, for example, consist of an envelope of black
735 shales, or fractures in an impermeable quartzite, mafic rock or older quartz vein. The high
736 fluid pressures generated by high temperatures, devolatilisation and a low permeability
737 envelope are essential for the development of high equilibrium solubilities of gold. It is
738 perhaps important that many large gold deposits are hosted in shale or pelite environments
739 (Wood and Popov, 2006; Wilson et al., 2009, 2013).
740 Orogenic gold systems resemble open flow packed bed chemical reactors (Aris, 1975;
741 Rawlings and Ekerdt, 2013, Chapter 7) in that there is a strong coupling between fluid flow,
742 thermal transport and chemical reactions. As such they are described by some form of
743 reaction-advection-diffusion equation as presented in (1). An important difference between
744 an orogenic gold system and a conventional fixed bed reactor of the chemical engineer is that
745 deformation is an important dissipative process that is absent in fixed bed chemical reactors.
746 Reaction-advection-diffusion equations generally lead to spatio-temporal patterning and the
747 results presented in this chapter are some examples of such patterning.
748 There is a special form of spatio-temporal behaviour that occurs in reaction-advection
749 systems where exothermic and endothermic reactions are coupled. These patterns, called
750 travelling waves, consist of strong localisations of temperature that move through the system
751 at speeds (the group velocity) that are generally less than the speed associated with a material
752 particle. In some cases the travelling wave localises into a soliton. Examples are given by

Ball et al. (1999), Hmaidi et al. (2010), Sharples et al. (2012) and Forbes (1997, 2013a, b). These thermal solitons differ from classical standing waves in water (Whitham, 1974) in that they "sweep-up" any smaller thermal anomalies as they move so that the temperature in the largest soliton increases as the system evolves (Forbes, 2013 a). We propose that this kind of thermal soliton is responsible for producing bonanza grades (ounces per ton) of gold in some deposits. A typical reaction-advection system that might be capable of thermal soliton behaviour is shown in Figure 12.13 (a) where either of the reactions

$$FeCO_3 + 2H_2S + 0.5\ O_2 \xrightarrow{k_1} FeS_2 + CO_2 + 2H_2O;\ (\text{exothermic, } \Delta H = -245.95\ KJ)$$

siderite + hydrogen sulfide + oxygen → pyrite + carbon dioxide + water

or,

$$CaFe(CO_3)_2 + 2H_2S + 0.5O_2 \rightarrow FeS_2 + CaCO_3 + CO_2 + 2H_2O;\ (\text{exothermic, } \Delta H = -245.43\ KJ)$$

ankerite + hydrogen sulfide + oxygen → pyrite + calcite + carbon dioxide + water

proceed at the same time as the deposition of gold from solution during temperature and fluid pressure drops expressed by

$$AuHS(H_2S)_3^{\ 0} + 0.5H_2 \xrightarrow{k_2} Au + 4H_2S \quad (\text{endothermic, } \Delta H = 105.5\ KJ)$$

gold complex in solution + hydrogen → gold(solid) + hydrogen sulfide

Here the H_2S produced by the deposition of gold (an endothermic process) is used to react with siderite to produce pyrite (an exothermic process). The pyrite forming process releases ≈ 246 KJ of heat which is used to amplify the gold deposition process which requires ≈ 106 KJ of heat. The remaining 140 KJ of heat can be used to increase the temperature and hence increase both the siderite to pyrite and gold deposition rates. This kind of coupled reaction system when coupled with advective transport leads to a thermal soliton where the pyrite production process proceeds in the tail of the soliton and drives the gold deposition process in the soliton front (Figure 12.13 b). This kind of process needs to be integrated into the episodic behaviour reported in the main body of this chapter.

A similar process involves the heat released by localised deformation (Figures 12.13 c, d) as gold in solution is advected into the high temperature spike associated with the deformation. The increased heat in the upstream tail of the spike is used to drive the endothermic gold deposition process in the downstream front of the spike. An example where such localisation processes may have operated is given by Fougerouse et al. (2016) for the Obuasi gold deposit. Here there is widespread evidence of remobilisation of gold associated with localised deformation at the scale of 1 km and at the cm-scale associated with crenulation cleavages. Early high grades of gold (5 to 6 g/ton) are associated with the exothermic reaction: H_2S + ankerite → arsenopyrite and synchronous pervasive deformation, whereas grades of 15 g/ton are associated with later localised deformation (Fougerouse et al. 2015; 2016 a, b).

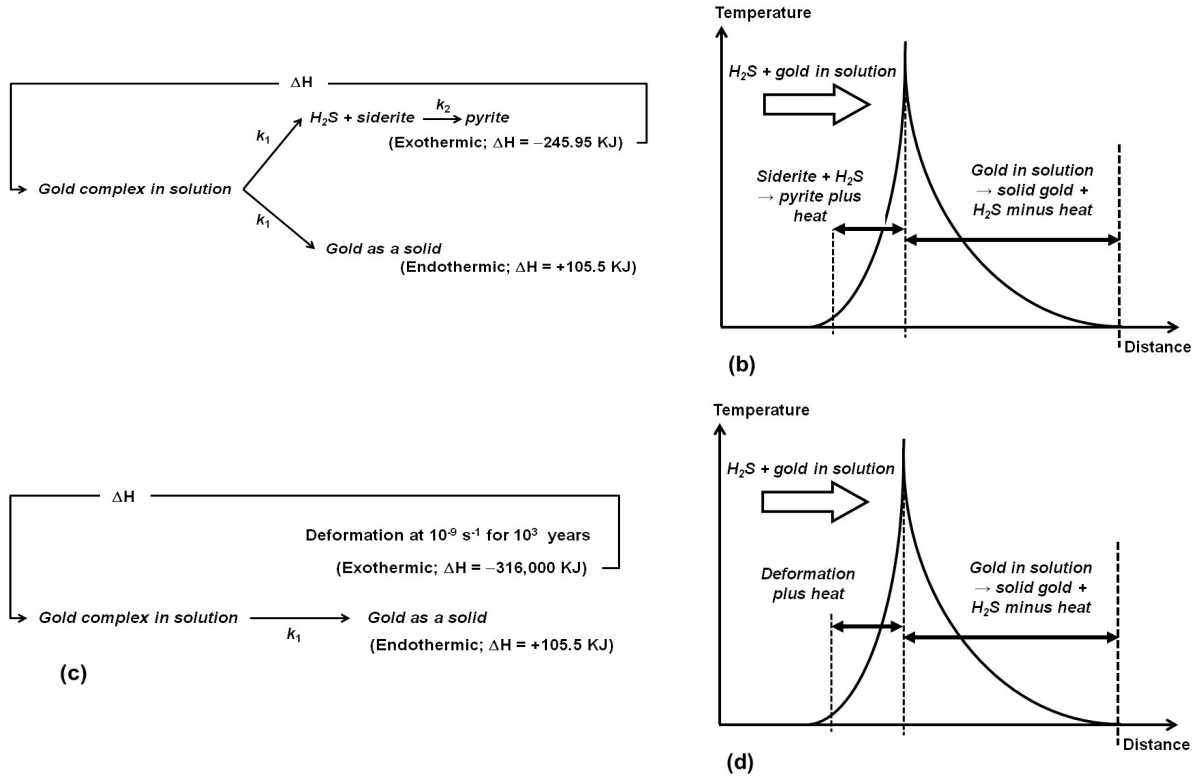


Figure 12.13. The development of thermal solitons. (a) Thermal feedback between gold deposition reaction and pyrite formation reactions. (b) Formation of a thermal soliton with spatial distributions of the siderite to pyrite reaction (exothermic) and the gold deposition reaction (endothermic). The direction of fluid flow is shown advecting H_2S and gold in solution. (c) Thermal feedback between gold deposition reaction and deformation. (d) Formation of a thermal soliton with spatial distributions of deformation (exothermic) and the gold deposition reaction (endothermic). The direction of fluid flow is shown advecting H_2S and gold in solution.

12.8. The implications of chaos.

The system we have described here behaves in an episodic but apparently stochastic manner in that the future of the system from any instant can only be predicted using probabilities. In addition, slight changes in operating conditions such as spatial position, permeability and thermal conductivity result in different behaviours. The stochastic behaviour and sensitivity to changes in operating conditions means that the system behaviour can be regarded as chaotic (Sprott, 2003). Even so the behaviour is the result of clearly defined physical and chemical rules so that the chaos is deterministic.

Systems that exhibit deterministic chaos commonly have two characteristic features. First, the large (in principle, infinite) number of states that the system occupies means that the system should be multifractal (Beck and Schlögl, 1993). These states are defined by temperature, fluid pressure, equilibrium gold solubility, gold in solution and deposited gold. Thus although the system evolves through a large number of states, some states occur more often than others. The frequencies of states are referred to as *singularities* and the intensity of the frequency is the *singularity strength*, commonly labelled, α (Feder, 1988). The chaotic nature of the system means (Beck and Schlögl, 1993) that the singularities occur in a manner such that each singularity strength is distributed in a fractal manner with its own fractal dimension, $f(\alpha)$. Thus the system can be thought of as a population of different singularities embedded in each other each with a different fractal dimension. Such a population is a

multifractal and can be represented as a singularity spectrum which is, from a statistical mechanics point of view, the entropy function for the system (Beck and Schlögl, 1993; Arneodo et al., 1995). In Figure 12.14 (a) we show the singularity spectrum for the temperature history shown in Figure 12.6 (a). The spectrum is well defined as is to be expected from a system exhibiting deterministic chaos.

The multifractal nature of the systems modelled in this chapter means that although the behaviour is chaotic, the system can be characterised by its singularity spectrum. Such spectra have different characteristics according to the physical and chemical processes that produced the system and can be symmetrical or asymmetrical, narrow or broad and have large or small values of the maximum value of $f(\alpha)$. We expect such multifractal detail to be represented in the spatial distribution of alteration and mineralisation in orogenic gold deposits as is indeed the case (see Chapters 6, 10 and 11). The data available to date indicate that small, less endowed orogenic gold systems have relatively narrow singularity spectra for gold abundances whereas larger, well-endowed deposits have wide asymmetrical singularity spectra.

The second feature of systems exhibiting deterministic chaos is that the various states of the system, although chaotic, are coupled so that not all states are possible or equally probable and those that do develop define an *attractor* for that particular system. An attractor is a representation of the solutions to the differential equations that describe the development and evolution of the system and hence contains information on the physical and chemical processes that formed the system. Some two dimensional versions of attractors are shown in Figures 12.9 (d) and 12.10 (d); a three dimensional attractor is shown in Figure 12.7 (c). Figure 12.14 (b) shows an attractor in (temperature – equilibrium gold solubility – gold in solution) – space for the system shown in Figure 12.6. The goal for the future is to develop such attractors for alteration assemblages and mineralisation in orogenic gold systems. In principle, large well-endowed systems should be characterised by different attractors than small, less-endowed systems.

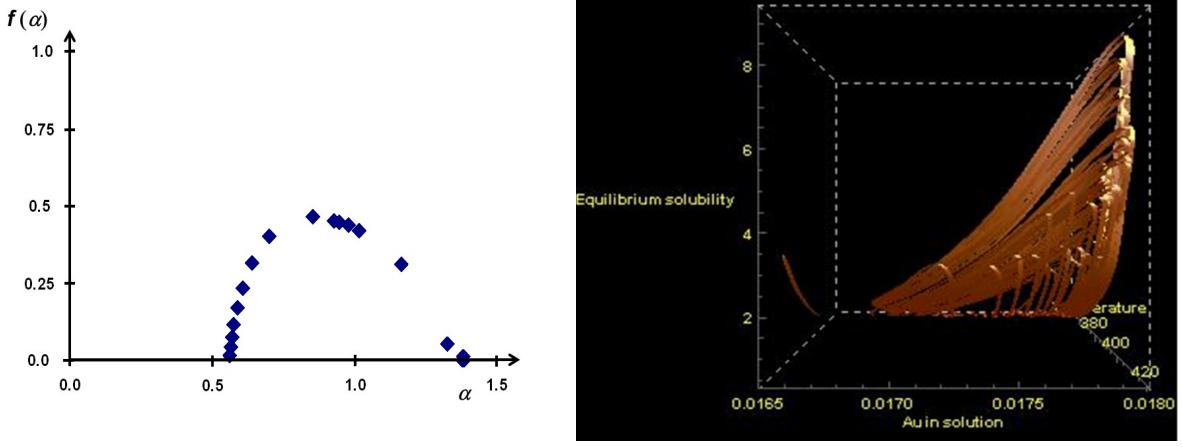


Figure 12.14. Chaos in system behaviour. (a) Multifractal spectrum for temperature history shown in Figure 6 (a). (b) Attractor in (temperature - gold in solution - equilibrium gold solubility) – space for system shown in Figure 8.

12.9. Conclusions.

Orogenic gold systems have been modelled as open flow thermodynamic systems in which the energy balance between deformation, exothermic and endothermic mineral reactions, fluid flow and heat transport is considered. The commonly observed episodic behaviour characteristic of orogenic gold systems comprising mineral zoning, crack-seal vein fabrics, overprinting brecciation events and multiple periods of gold deposition emerges from aseismic processes operating intrinsically to the system rather than as arising from seismic events extrinsic to the system. Oscillations in temperature, pore fluid pressure and the equilibrium solubilities of gold, quartz and other minerals are the direct result of competition between the energy and nutrients consumed by chemical reactions and the net supply of energy and nutrients in the incoming and outgoing fluid streams. This intrinsic behaviour of course does not rule out the influence of externally imposed adiabatic seismic events but it is important to realise that orogenic gold systems with their attendant coupling between chemical, hydraulic, mechanical and thermal processes are intrinsically unstable and oscillate in temperature and pore pressure in non-adiabatic manners. Any external forcing by episodic seismic activity can potentially couple with the intrinsic instabilities and reinforce them to enhance gold deposition. It is an open question as to the relative importance of intrinsic and extrinsic influences on the behaviour of orogenic gold systems. The intrinsic behaviour reported here is on a much longer time scale than extrinsic seismic coupling.

Assuming that the incoming fluid carries gold at a concentration of a few parts per billion by weight of fluid, gold grades of a few parts per million by weight of the rock can be generated by the episodic partial dissolution and deposition of both the dissolved gold and the incoming gold in solution over a period of 100,000 to 500,000 years. Although high temperatures are important for high gold grades to develop, another critical control on the gold grade for a given temperature arises from processes that increase the fluid pressure of the system. These processes relate to low permeability and low thermal conductivity of the country rocks. Low country rock permeability and thermal conductivity lead to higher internal pore pressures and hence higher equilibrium gold solubilities and ultimately higher deposited gold grades. Bonanza gold grades (ounces per tonne) in general require processes that localise gold concentrations involving coupling between strongly exothermic processes such as the H_2S + siderite/ankerite → pyrite reaction and the endothermic reaction: $gold^{(solution)} \rightarrow gold^{(solid)} + H_2S$. Such coupling results in thermal solitons that sweep up (remobilise) deposited gold and localise gold deposition.

A fundamental conclusion, commonly neglected but fundamental to targeting of high grade orogenic gold deposits, is that all of the processes that lead to high gold grades can be read from the energy balance of the system recorded by the paragenetic sequence and its relation both spatially and temporally to deformation. Such data is readily available in drill core and outcrop and becomes an important mineral exploration tool in deciding if a particular deposit is likely to be of high grade.