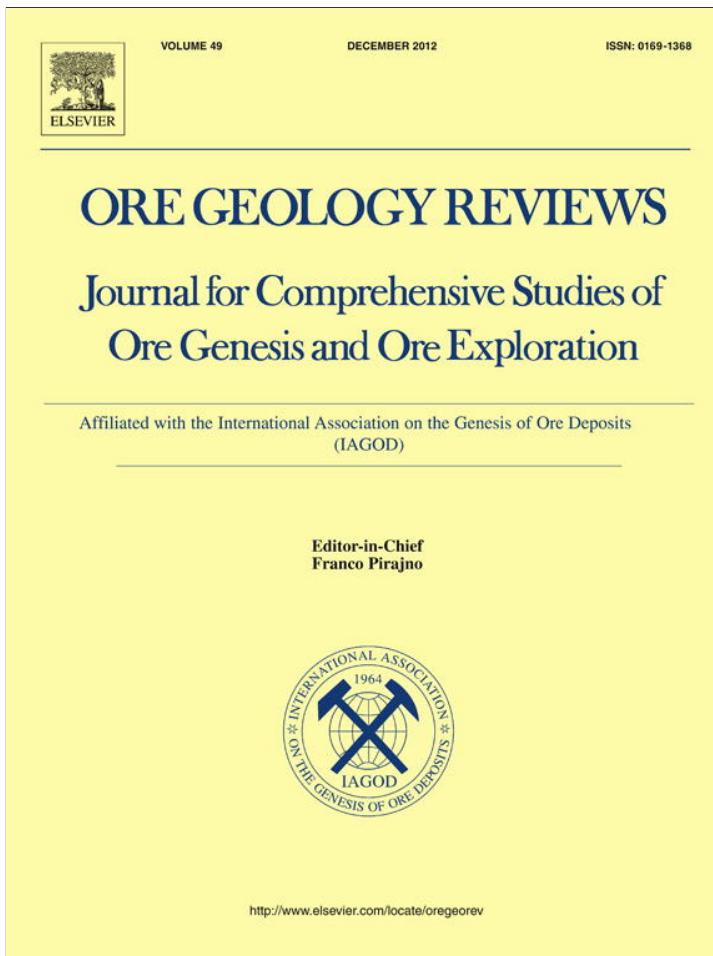


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Review

The mechanics of hydrothermal systems: I. Ore systems as chemical reactors

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ABSTRACT

The formation of giant hydrothermal ore bodies is a metasomatic process whereby the influx of heat and of large volumes of fluids results in chemical reactions both within the fluids and between the fluids and the rock mass. The result is the development of relatively large volumes of altered mineral assemblages and relatively small, commonly localised, volumes of valuable minerals. This paper and its sequel treat such hydrothermal mineralising systems as open flow chemical reactors and review the concepts that are pertinent to understanding how such reactors operate to optimise the concentrations of valuable minerals such as sulphides and metals. Non-equilibrium theories of open flow reacting systems are the basis for such optimisation. Contrary to popular fashion in the geosciences it is possible to operate open flow reactors far from equilibrium indefinitely as long as the relevant supply of reactants and energy is fed to the system. Even the simplest of chemical reactions, a first order exothermic reaction, A→B, is unstable and produces a rich variety of relations between reaction rate and the rate of supply of reactants together with oscillations in temperature and chemical composition during the life of the reactor. Such instabilities are enhanced by processes involving autocatalysis and/or heterogeneous reaction kinetics. These instabilities lead to oscillations in temperature, Eh and pH in both space and time and constitute the essential mechanisms responsible for sulphide/metal deposition and for mineral and compositional zonation within the system. Their behaviour is critically dependent on the local permeability. Many alteration reactions are exothermic and are self enhancing whilst the initial alteration proceeds. During such a stage hydrothermal mineralising systems are open exothermic chemical reactors that operate to develop the alteration system, veining and brecciation. The deposition of sulphides, metals and many silicates is an endothermic process that tends to quench the system. The size and grade of a particular mineral deposit is a play-off between these exothermic and endothermic processes and is reflected in the paragenetic sequence and in both the gross and detailed structural evolution of the hydrothermal system. The latter stages of evolution of successful mineral systems are characterised by competition between exothermic and endothermic processes in which the chemical systems are autocatalytic in H⁺. This competitive behaviour is the hallmark of a successful mineral system. The fundamental roles of extrema entropy production principles are explored to define the evolution and characteristics of hydrothermal systems. In this first paper (Part I) we outline the basic theory behind such processes and concentrate on the coupling between deformation, fluid transport, heat (entropy) production and chemical reactions. In the sequel (Part II) we examine the processes that lead to efficient mixing of fluids and the role that such mixing processes play in enhancing mineral reactions, in controlling their spatial relations and in producing multifractal ore grade distributions.

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1. Introduction

This paper is concerned with the mechanics of hydrothermal systems. The subject called *mechanics* is the study of the response of materials to applied forces or applied displacements on the boundaries of the material. This response depends on many physical and chemical factors one of which is the nature of the chemical reactions taking place. In this particular instance the nature of the chemical reactions influences the fracture behaviour of the system; this in turn influences the nature of the chemical reactions. Many models of the hydrothermal process adopt a linear approach that implicitly or explicitly assumes that the system possesses only one stationary state, namely an equilibrium state. The term *stationary state* refers to that state of a system where the *mean* value of some property such as chemical concentration, temperature or fluid flow rate does not change with time. *Equilibrium* is one such stationary state but others correspond to situations where the mean value of the property is time invariant. This does not carry the connotation that there is no variability in the property. Steady, oscillatory and/or chaotic behaviour may characterise the behaviour near the stationary state so long as the mean value is constant. Further, the assumption is commonly made that even though the system is open to the flow of heat and mass the residence time of an element of fluid is large compared to the characteristic times of mineralising processes such as chemical reactions, heat flow and deformation. This is taken to mean that the *assumption of local equilibrium* (Korzhinskii, 1950; Thompson, 1959, 1970) follows so that at each point in the rock mass at a particular time the system can be assumed to be at equilibrium implying that the situation is isothermal and the effects of energy dissipation arising from chemical reactions, fluid flow and deformation on the evolution of the system and on the nature and spatial distribution of mineral assemblages can be neglected. These assumptions are only true for *closed linear systems* and the behaviour can become more complicated and even counter-intuitive if the system is both nonlinear and open. The basic concepts behind the behaviour of open systems were recognised by Korzhinskii (1950, 1965, 1966, 1967) and we will show that much of his discussion holds

independently of an assumption of local equilibrium. Many nonlinear systems possess multiple non-equilibrium stationary states (Cross and Greenside, 2009; Epstein and Pojman, 1998; Gray and Scott, 1990). In this paper we review work on nonlinear, *open flow* hydrothermal systems with the implication that the systems may be characterised by such multiple non-equilibrium stationary states. We discuss the meaning of the term *nonlinear system* in Section 4.3. The term *open flow* refers to a thermodynamically open system where both mass and heat can enter and leave the system in some defined (and hence constrained) manner. Even the simplest of open flow chemical systems involving just one uncatalysed, first order, reversible, exothermic reaction described by $A \rightleftharpoons B$, falls into this category, the nonlinearity being created by competition between the net flow rates (the rates at which A and B are added to the system) and thermal feedback on the reaction rate. Fluid flow, deformation and some chemical reactions involving autocatalytic processes (Epstein and Pojman, 1998), chain branching (Gray and Scott, 1990), and coupled heterogeneous reactions (Ertl, 2009; Imbihl, 2009; Imbihl and Ertl, 1995; Libuda et al., 2005; Saliccioli et al., 2011), induce instability in nonlinear systems so that spatial and/or temporal patterns in chemical composition are the norm. In particular these patterns can involve large spatial and/or temporal fluctuations in Eh and pH with accompanied fluctuations in the deposition of sulphides, iron oxides and metals such as gold. These fluctuations represent oscillations about non-equilibrium stationary states. In some systems one stationary state is relatively close to equilibrium and is sometimes called the *thermodynamic branch*. In other systems the stationary states remain far from equilibrium and some represent conditions for enhanced precipitation of metals and sulphides. Most importantly, the spatial coexistence of both states in the same body of metasomatised rock can arise solely from slight fluctuations in flow rate (Gray and Scott, 1990) and hence in permeability. The fundamental issue for the mineral explorationist is to identify which state is represented by an individual body of rock. This involves first understanding the basic modes of behaviour of open flow reacting systems and then adopting a holistic view of the metasomatic system and identifying those signals that herald a transition from one mode of

behaviour to another non-equilibrium mode of the system. A useful exercise for the explorationist is systematically to design a chemical reactor with the goal of identifying those critical parameters that will produce the mineralising system of interest in the optimal manner. Some conceptual models of hydrothermal systems viewed as open chemical reactors held far from equilibrium by the influx of mass and heat are shown in Fig. 1.1.

Non-equilibrium thermodynamics is the natural language of open flow reacting systems. For the purposes of this paper we define *thermodynamics* as: *the study of the flow of physical and chemical quantities through a system under the influence of thermodynamic forces*. The physical and chemical quantities relevant to hydrothermal systems are momentum (per unit area), mass, fluid and heat. The respective thermodynamic forces (also called *affinities*) comprise the gradients in deformation, chemical potential, hydraulic potential and temperature (Coussy, 1995, 2004; Truesdell, 1966a). The classical view of chemical equilibrium thermodynamics assumes that the thermodynamic forces are all zero and hence the flows of all physical and chemical quantities are zero.

The aim of this review is to explore the origin of the characteristics of mineralised hydrothermal systems within a non-equilibrium framework that couples mineral reactions with fluid flow in such systems. The importance lies in the potential that such an understanding will lead to a rational basis for defining (i) vectors to mineralisation within the alteration envelope outside of the ore-body; (ii) criteria for deciding on the size of the ore system from limited data; (iii) criteria for deciding on the grade of the deposit from limited data; and (iv) use of the multi-fractal character of the deposit to improve estimation of ore grade. The framework has direct application to any open fluid infiltration system including the type explored by Korzhinskii (1950, see Reverdatto, 2010) and Thompson (1970, 1959) but extends that work to concentrate on non-equilibrium aspects of the processes that operate in alteration/mineralising systems.

Hydrothermal ore deposits form by the infiltration of metal bearing fluids into a chemically reactive environment that enables the metals or metal bearing minerals to be precipitated. In the same hydrothermal event these fluids are responsible for alteration of the surrounding rock on a spatial scale that may be up to many tens of kilometres in extent. In many instances the site for metal precipitation is undergoing active plastic deformation and/or fracturing/brecciation at the time of alteration/mineralisation. The chemical reactions taking place in the ore body and within the alteration envelope are commonly networked (in the sense of Carmichael, 1969) so that the products of one reaction act as reactants for least one other reaction. An example is the set of reactions in Eq. (1.1):

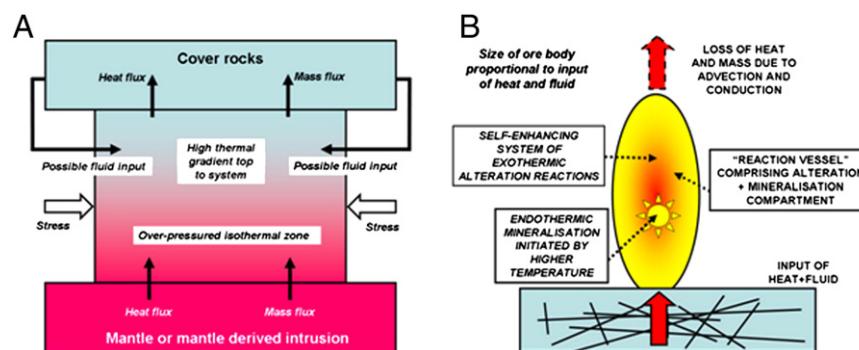
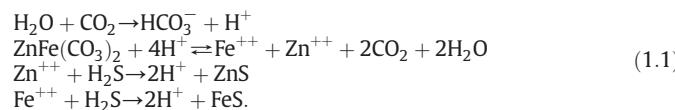


Fig. 1.1. Some models of hydrothermal systems viewed as open flow chemical reactors held far from equilibrium by the influx of mass and heat.

Here, H^+ is produced by the flux of CO_2 and is then used to generate Fe^{++} and Zn^{++} . Reaction of these ions with H_2S then generates even more H^+ . Reactions of this type have been considered by Anderson and Garven (1987). It should be noted that the set of reactions (1.1) is autocatalytic in H^+ and the concentration of CO_2 depends in a nonlinear manner on the pH (Section 7). Such relations are neglected in an equilibrium approach.

The problem therefore is one involving networked reaction-diffusion processes with coupled advection by fluid flow and deformation within a porous medium where the porosity is continuously evolving due to mechanical and/or chemical damage (Fig. 1.2). In addition the mineral reactions involving the formation of carbonates and hydrous phases, such as muscovite, chlorite and pyrophyllite, and of iron oxides that occur in the alteration envelope are commonly exothermal (Haack and Zimmermann, 1996; Norton and Cathles, 1979). Since the rates of chemical reactions are exponentially dependent on temperature the alteration process is self-enhancing (or thermo-catalytic, Putnis, 2002, 2009) in the sense that the faster alteration occurs the more intense the process becomes. The processes operating within the alteration system resemble therefore those occurring in an explosion and the mathematical behaviour has close affinities with the mathematics of combustion (Gray and Scott, 1990; Law, 2006). The precipitation of sulphides and many silicates is endothermic (Norton and Cathles, 1979; Peacock, 1987) and tends to quench the system. Since the initiation of the K^{th} chemical reaction (Law, 2006) depends on the ratio of $\frac{E^k}{R}$ to T , where E^k is the activation energy of the K^{th} reaction, R is the gas constant and T is the local absolute temperature of the system, we see here one origin for the paragenetic sequence. The situation is strongly nonlinear since the reaction rate is commonly a function of temperature and of Eh and pH (Lasaga, 1984; Rochelle and Turner, 2005). The time taken to arrive at conditions where quenching of the system is more important than the heat released by the development of hydrous alteration phases, is one of the factors that governs the ultimate size and grade of the deposit. Even so, for a mineralising system which is flow controlled to be really large, processes must continue to accommodate the relentless supply of fluid at a given temperature and composition and this is commonly accomplished by other exothermic processes such as sliding on fractures during fracturing, brecciation and stockwork formation. Giant hydrothermal ore systems are chemical reaction vessels held far from equilibrium by the influx (and efflux) of heat and mass. Such systems can be addressed with a lot of mathematics. Here we want to distill the mathematics into some simple working principles. If one can understand and apply these principles the opportunity exists to recognise, with limited data, whether one is in a successful or failed system and where next to explore in the system if it has the hallmarks of a successful system. The conditions necessary for a hydrothermal system to succeed as a highly mineralised system are expressed by Bejan and Lorente (2010) in the form of their *Constructal Law* which they claim is a fundamental law of Nature: *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*. Independently of whether this statement really is a fundamental law of nature

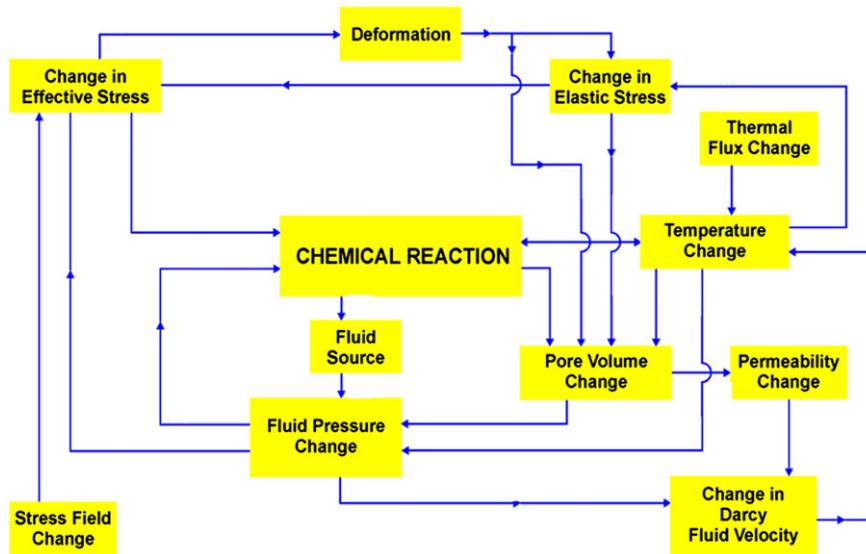


Fig. 1.2. Some feedback relations in the fully coupled deformation-thermal-fluid-chemical system.

the statement does describe the competitive nature of the evolutionary processes that are observed in successful mineral systems; we will discuss this evolution in terms of entropy production principles in Section 8. We also show that this condition is responsible for the multifractal nature of mineralised systems including the distribution of ore grades.

Problems of this type have been considered by various authors but rarely with a view to integrating all of the processes involved in the coupled problem and rarely with the concept of an open flow chemical reactor in mind. Ingebritsen et al. (2010) have discussed some recent advances in computer modelling such systems particularly with respect to the incorporation of multi-phase flow. Steefel and Lasaga (1994) and Steefel and Maher (2009) review much of the work on fluid–rock interaction during reaction–transport processes and discuss the concept and relevance of “local equilibrium”. Ortoleva and co-workers (Ortoleva, 1994; Ortoleva et al., 1987a) have addressed the coupled reaction–diffusion–advection problem and, in various forms, the reaction–diffusion–deformation problem (Ortoleva, 1989, 1994; Ortoleva and Ross, 1973, 1974). In this large and important body of work full coupling of chemical reactions to fluid properties such as viscosity and density is not addressed from an analytical point of view. Tel et al. (2005) have reviewed the reaction–diffusion–advection problem with an emphasis on the chaotic flow of fluids and this aspect is considered in Part II. Chaotic flow is a term given to unsteady laminar (*not turbulent*) flow where adjacent packages of fluid do not remain adjacent as the flow progresses. This latter work is important since it emphasises the very significant effect of chaotic flow in enhancing fluid mixing, and in producing multifractal distributions of reaction sites as well as an enormous enhancement (up to a factor of 10^6) of local reaction rates. A reaction–diffusion system with some coupling to fluid advection has been addressed specifically for mineralising systems by Rusinov and Zhukov (2000, 2008). A deforming system with coupled thermal and chemical effects is considered by Veveakis et al. (2010). Reaction–advection flows in porous media in which the chemical reactions are exothermic and thermal effects are coupled to changes in fluid viscosity, density and surface tension have been addressed in a large number of recent papers (Almarcha et al., 2010a, 2010b; Bansagi et al., 2003, 2011; De Wit, 2001, 2004, 2008; De Wit et al., 2003; D'Hernoncourt and De Wit, 2010; D'Hernoncourt et al., 2006, 2007; Lima et al., 2006; Rongy and De Wit, 2009; Rongy et al., 2007). Open flow reacting systems have been considered by Bejan (2007; Bejan and Lorente, 2006) and Niven (2009, 2010b; Niven and Andresen, 2010). The concept of mineralising systems as critical systems has been

discussed by Hronsky (2010, 2011). Of particular relevance are direct studies of non-equilibrium processes as features of hydrothermal systems (Berger and Henley, 2011; Henley and Berger, 2000, 2011). These particular papers highlight many aspects of what is considered from a wider viewpoint here, namely, the role of feedback between physical and chemical processes in generating nonlinear behaviour and complexity, the importance of considering the heat (entropy) budget in hydrothermal systems, the possibility of oscillations in temperature and of Eh in a reacting but otherwise homogeneous, pre-mixed fluid and the importance of localised flow (generated by deformation) in influencing chemical reactions in the system. We will show that these aspects of hydrothermal systems derive directly from the second law of thermodynamics and are an expression of the Constructal Law of Bejan and Lorente (2006, 2010). The above literature is scattered over the geological, physical chemistry, chemical engineering, thermodynamics and solid mechanics literature. The intent of this review is not to undertake an in-depth analysis of the non-equilibrium characteristics of hydrothermal systems (some of which are considered by Berger and Henley, 2011; Henley and Berger, 2000, 2011) but to bring some of the relevant work on non-equilibrium behaviour together into one place and to attempt a synthesis in terms of a coherent framework based on non-equilibrium thermodynamics. Clearly the literature is immense and we have selected only those papers that illustrate important examples or principles.

Mineral reactions in hydrothermal systems commonly involve replacement and/or pseudomorphic processes which preserve the volume of material during the reaction (Bastin, 1950; Bastin et al., 1931; Lindgren, 1912, 1918, 1925, 1933; Merino and Canals, 2011). Thus the reactions should be written such as to conserve volume rather than the traditional way that conserves mass. There has been considerable discussion on this matter (Carmichael, 1987; Korzhinskii, 1968, 1970; Merino and Canals, 2011; Ridge, 1949; Vernon, 1978, 1979; Vernon and Clarke, 2008; Vernon and Pooley, 1981) and great reluctance within the metamorphic–metasomatic community to accept the proposition of constant volume replacement since such acceptance significantly alters the nature of the reactions and calls into question whether the pressure is constant during the reaction. In particular, Carmichael (1987) has proposed that the reactions begin as constant volume but that the stresses generated during such a reaction arising from the ΔV of the reaction drive secondary diffusion that relaxes the stress to hydrostatic and ultimately produces a net reaction that is equivalent to constant mass. The postulate of constant volume reactions (which is what is actually observed) results in nonlinear feedback relations (Fletcher and Merino, 2001; Merino and Canals, 2011) that lead to

oscillatory growth of grains and vein fillings and that explain much of what is observed especially in the case of replacement of calcite by dolomite (Merino and Canals, 2011). The whole issue of replacement/pseudomorphism in hydrothermal reactions is a subject of considerable importance and is worthy of future emphasis. In this paper, in reviewing the available literature, we report on the conventional approach that always involves the assumption of constant mass.

The plan of the review is as follows: In Section 2 we define some terms and set out the governing equations for open flow chemically reacting systems; we take the opportunity to state the ways in which the approach taken here differs from previous approaches in the geosciences. In Section 3 we outline the geological characteristics of some hydrothermal mineralised systems with an emphasis on those characteristics important for viewing the system as an open flow chemical reactor operating far from equilibrium. These characteristics include strong spatial gradients in chemical potential, specifically expressed as redox/pH fronts, as well as patterning at spatial scales ranging over 15 orders of magnitude. Examples are described *inter alia* from the gold systems of Western Australia and the Witwatersrand and from the IOCG deposit at Olympic Dam.

In Section 4 we clarify terminology further and the overall approach to nonlinear systems by considering the various processes and mechanisms that operate in hydrothermal systems. A general approach is taken where equilibrium is not assumed, coupling exists between reactions, and between reactions and fluid flow, and the chemical system is nonlinear. This enables us to discuss the behaviour of some nonlinear hydrothermal systems with an emphasis on the way in which such behaviour is related to but differs from the classical *local equilibrium* approach which assumes steady flow, isothermal reactions, no kinetic coupling between reactions, and linear chemical systems. In particular we point to recent developments involving extrema entropy production principles for open flow reacting systems that have the potential to greatly simplify the treatment of such systems. In Section 5 we explore aspects of the plumbing system for hydrothermal systems with respect to controls on the fluid flux, the permeability and brecciation processes and the residence time of fluids. In Section 6 we elaborate upon the various types of reactions that can occur in open flow systems and point out that for even the simplest of chemical systems the behaviour is non-linear if the heats of reaction are included. The results of this exploration are complex responses where temporal and spatial patterns of chemical composition emerge spontaneously from initially well mixed systems. These patterns include spatial and temporal patterns of Eh and pH. Although mixing of two or more distinct fluids is considered such a process is not necessary to produce the Eh–pH gradients we see in hydrothermal systems as has been emphasised by Berger and Henley (2011) and Henley and Berger (2000, 2011) for epithermal systems. In Section 7 we explore other chemical mechanisms of producing nonlinear behaviour and instability including autocatalysis and heterogeneous kinetics. We close Part I (Sections 8 and 9) with some discussion and concluding remarks of relevance to mineral exploration.

Mixing of two or more fluids of completely different sources has been widely proposed to account for observed gradients in Eh and pH in mineralised systems (Appold and Garven, 2000; Neumayr et al., 2005, 2008; Prendergast, 2007), but see also Evans (2010). The challenge is to understand such mixing effects over large ranges of spatial scales. We discuss the issues associated with the mixing of two reacting fluids in Part II where we emphasise that some form of chaotic flow is necessary to produce efficient mixing and significantly enhanced reaction rates. Since steady Darcian flows can never be chaotic (Sposito, 1994, 2001, 2006) mechanisms for the generation of non-steady flows are necessary to promote efficient fluid mixing. In Part II we examine various ways of enhancing chemical reaction rates including coupling chemical reactions with the physical properties of the fluid and the development of chaotic mixing systems in open pore spaces and

fracture networks. Such work is relevant to the assumptions made in geostatistical analyses of ore grade (Cressie, 1993).

This paper is referred to as Part I and the sequel as Part II. Terms and symbols are defined as they are first used and in Table A1 in the Appendix. Some equations are repeated in slightly different forms in various sections and in both parts so that each section is more or less independent of other sections.

2. Governing equations and definition of terms

There is an extensive literature concerned with modelling fluid transport in porous rocks with coupled chemical reactions and fluid transport coupled with dissolution and precipitation. An important recent review with an historical summary is Steefel and Maher (2009) and the overall approach is considered by Steefel and Lasaga (1994). Another important approach is that of Bethke (1996), Grichuk and Shvarov (2002) and Reed (1997, 1998) where the extent (or progress) of a reaction is simulated by a series of steps each one of which is taken to be in *local equilibrium*. This attempts to reproduce the approach discussed by Thompson (1970, 1959).

The governing equations linking the rate of change of chemical composition with changes in composition arising from advection and reaction rates are commonly written:

$$\frac{\partial(\phi c_i)}{\partial t} + \mathbf{J} \cdot \nabla c_i = R_i \quad (2.1)$$

where c_i is the concentration of the i^{th} chemical species in solution (with units moles per unit volume of the fluid), ϕ is the instantaneous porosity, \mathbf{J} is the sum of the fluxes (moles per unit area of the rock per unit time) that arise from dispersive, diffusive and advective processes, ∇ is the gradient operator, \cdot represents the scalar product and R_i is the total reaction rate (moles per unit volume of the rock per unit time) for the reaction involving the i^{th} chemical species and may be expressed as:

$$R_i = R_i^{\text{homogeneous}} + R_i^{\text{heterogeneous}}. \quad (2.2)$$

$R_i^{\text{homogeneous}}$ is the reaction rate of the i^{th} reaction occurring in solution and $R_i^{\text{heterogeneous}}$ is the reaction rate of the i^{th} reaction occurring at solid/liquid interfaces. Typically $R_i^{\text{heterogeneous}}$ is a function of the surface area of the reacting grain and of pH (Lasaga, 1981, 1984). Heterogeneous reactions are considered in Section 7.

A common approach (Phillips, 1991, 2009; Wood and Hewett, 1982) to using Eq. (2.1) is to assume equilibrium, so that one can neglect the term R_i in Eq. (2.1), and c_i then represents the equilibrium concentration of the species C_i in solution. The porosity is assumed to remain constant and one writes

$$c_i^{\text{equilibrium}} = c_i \left(P^{\text{fluid}}, T, c_{\kappa} \right) \quad (2.3)$$

where κ is the number of species. Using the chain rule of differentiation it follows that:

$$\phi \frac{\partial c_i}{\partial t} = -\mathbf{J} \cdot \left\{ \frac{\partial c_i}{\partial T} \nabla T + \frac{\partial c_i}{\partial P^{\text{fluid}}} \nabla P^{\text{fluid}} + \sum_{k=1}^{\kappa} \frac{\partial c_i}{\partial c_k} \nabla c_k \right\}. \quad (2.4)$$

Clearly the assumptions involved here (equilibrium and constant porosity) are extreme but nevertheless the approach has a wide following (Murphy et al., 2008; Phillips, 1991, 2009; Steefel et al., 2005; Wood and Hewett, 1982; Zhang et al., 2003b, 2008; Zhao et al., 2009).

The problem is formulated in this paper with reference to Figs. 1.2 and 2.1. In Fig. 2.1(a) a body of rock of length L and cross-sectional area Σ has an instantaneous porosity, ϕ and permeability K . This body of rock can be referred to as the *control volume* (Niven,

2009). Commonly the porosity and permeability are related by the Carman–Kozeny formula (Nield and Bejan, 1992):

$$K = \frac{K_0(1-\phi_0)^2\phi^3}{\phi_0^2(1-\phi)^2} \quad (2.5)$$

where K is the current permeability at porosity ϕ , and K_0 is the permeability at porosity ϕ_0 . The flux of fluid through the rock is given by Darcy's law:

$$\hat{\mathbf{V}} = -\frac{K}{\mu}(\nabla p^{\text{fluid}} - \rho^{\text{fluid}} \mathbf{g}) \quad (2.6)$$

where $\hat{\mathbf{V}}$ is the Darcy flux ($\text{m}^3 \text{ m}^{-2} \text{ s}^{-1}$), μ is the fluid viscosity (Pa s), p^{fluid} is the fluid pressure (Pa), ρ^{fluid} is the density of the fluid (kg m^{-3}) and \mathbf{g} is the acceleration due to gravity (m s^{-2}). In Section 5 we will find it convenient to write Eq. (2.6) with K as the dependent variable instead of $\hat{\mathbf{V}}$. Multi-phase flow is expressed as an extension of Eq. (2.6) (see Ingebritsen et al., 2010); we consider only single phase flow in this paper. We also assume that the permeability is isotropic.

Mass conservation is expressed (Phillips, 2009, p 13) as

$$\frac{\partial(\phi\rho)}{\partial t} + \nabla \cdot (\rho\hat{\mathbf{V}}) = \rho^{\text{fluid}} S^{\text{fluid}} \quad (2.7)$$

where the term $\rho^{\text{fluid}} S^{\text{fluid}}$ represents the rate of generation of fluid by mineral reactions per unit volume of rock. ρ^{fluid} is the density of the interstitial fluid and S^{fluid} is the rate of production of fluid. It is important to note when dealing with chemical reactions that it is mass that is conserved and not moles of a particular species so the units considered need to take this into account (Fitts, 1962, p 7).

Since c_i is the concentration of the chemical species C_i , with units of moles per cubic metres of solution in the rock, the concentration of C_i per total volume of the rock mass is ϕc_i . $V = \Sigma L$ is the total volume of the control volume. Chemical species are added to the rock mass via a volumetric flow q with units $\text{m}^3 \text{ s}^{-1}$ so that the Darcy flux, $\hat{\mathbf{V}}$,

is $\hat{\mathbf{V}} = \frac{q\phi}{\Sigma}$ with units $\text{m}^3 \text{ m}^{-2} \text{ s}^{-1}$. The actual velocity of the fluid is $\hat{\mathbf{V}}/\phi$. The residence time is

$$\tau = \frac{V}{q} = \frac{L\phi}{\hat{V}}. \quad (2.8)$$

For open flow systems it is convenient (Borckmans et al., 2002; Gray and Scott, 1990; Pojman, 1990) to rewrite Eq. (2.1) as:

Total rate of production of C_i	=	Rate of production of C_i by chemical reactions in the box	+	Rate of addition of C_i at inlet minus removal of C_i at outlet	+	Rate of addition of C_i by diffusion
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$$\frac{\partial(\phi c_i)}{\partial t} = \sum_{k=1}^{\infty} R_k(c_i, \bar{\lambda}_k) + q\phi(c_i^0 - c_i) + \phi D_i \nabla^2 c_i \quad (2.9)$$

where D_i is the diffusion coefficient for C_i , c_i^0 is the inlet concentration of C_i , $\bar{\lambda}_k$ is a parameter that controls the behaviour of the reaction, R_k , and ∇ is the gradient operator. The departures in this paper from the classical ways of treating reaction–transport–diffusion processes in the geosciences lie in: (i) the expression of the coupling between transport, reaction and diffusion in the form of Eq. (2.9) rather than Eq. (2.1); Eq. (2.9) presents a powerful method of readily identifying non-equilibrium stationary states in even the most complicated chemical reactions as has been discussed in depth by Gray and Scott (1990). (ii) The recognition that various forms of feedback processes (heat generated by reactions, autocatalysis and heterogeneous kinetics) means that Eq. (2.9) has more than one non-equilibrium stationary state and these states may be stable or unstable. (iii) A realisation that Eq. (2.9) is nonlinear and that the solutions to Eq. (2.9) can be periodic both spatially and temporally or even chaotic. In an important class of reactions, of which exothermic reactions are an example, the net rate of flow represented by the second box on the right hand side of Eq. (2.9) can be a nonlinear function of the residence time, τ , thus introducing considerable complexity into a system with constant input flux, q , depending on subtle variations in ϕ and hence the permeability (Gray and Scott, 1990).

In addition, constitutive laws or equations of state are required that express the dependence of the physical properties of the fluid in terms of physical and chemical conditions. Thus we need expressions such as

$$\mu = \mu(p^{\text{fluid}}, T, c_i), \rho^{\text{fluid}} = \rho(p^{\text{fluid}}, T, c_i).$$

Deformation is an important part of the coupling depicted in Fig. 1.2 but we do not emphasise that aspect of the problem in this paper except to note that fracturing and, in particular, brecciation is an important mechanism for generating permeability in a flow controlled system. Relevant mechanical constitutive relations and their coupling to chemical processes are given by Coussy (1995, 2004), Coussy and Ulm (1996) and Housby and Puzrin (2006).

Fracturing, veining and brecciation are fundamental processes operating within hydrothermal systems (Cox, 1995, 1999; Cox et al., 2001; Sibson, 1987, 1992), but very little published material exists with respect to a quantitative discussion, in terms of constitutive behaviour, of how these processes operate within hydrothermal systems. The classical theories of fracture proposed by Barenblatt (1962) and Griffith (1921) assume a convex Helmholtz energy together with concave form of surface energies and have been very successful in explaining many aspects of fracture development. However they have not been very successful in describing the evolution of fracture

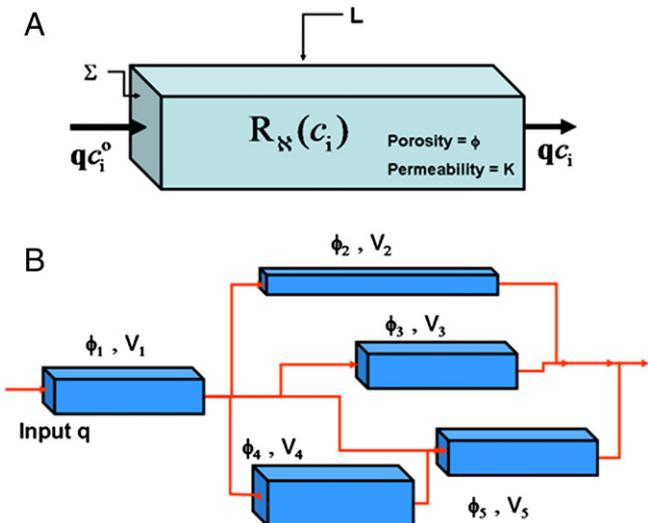


Fig. 2.1. Model of an open flow-controlled hydrothermal system. (A) The system with cross-sectional area, Σ , and length, L . The body of rock represented in (A) is the control volume. The input fluid has a flow rate of $q \text{ m}^3 \text{ s}^{-1}$ and contains i chemical species within the unit with rates $R_n \text{ mol s}^{-1}$. The control volume has a porosity ϕ and a permeability K . (B) Within the control volume there may exist a network of units, that make up the entire hydrothermal system, connected both in parallel and in series each with different porosities and permeabilities.

systems (including in particular, fracture patterns) and of brecciation. The new generation of fracture theories is based on non-convex Helmholtz energies (Del Piero and Truskinovsky, 2001). These new non-convex theories explain the development of more complicated fracture arrays but to date such approaches have not formed a basis for understanding the fracture patterns so widespread in naturally deformed rocks. Such theories however do highlight the role of criticality in the development of fracture systems. The term *criticality* is used here in its classical sense (Sornette, 2000), and not in the sense of self-organised criticality of Bak (1996). Classical criticality refers to the behaviour of a system controlled by a parameter that, for a critical value, marks the emergence of a phase transition where the Helmholtz energy passes from convex to non-convex (Ben-Zion, 2008). Such critical phenomena are commonly associated with a fractal distribution of structure (Hobbs et al., 2011). Self-organised criticality refers to a transition from a stable to an unstable state produced by the steady evolution of a parameter. Again, fractal geometries emerge. It is not yet clear whether processes such as brecciation and veining represent classical criticality or self-organised criticality although Hronsky (2010, 2011) suggests the latter. Some recent discussions of fracturing and the transition from un-fractured to brecciated material based on non-equilibrium thermodynamics are given by Lyakhovsky et al. (2011) and Nguyen and Einav (2009). Another approach to this subject, which treats cracks as defects and formulates their interactions in terms of coupled reaction-diffusion equations, is given by Ord and Hobbs (2011). Experimental observations of the temperature evolution during fracturing and subsequent sliding are given in a series of papers by Wu and co-workers (Liu et al., 2006; Wu et al., 2006a, 2006b). They show that the loading process to failure is normally associated with a small increase in temperature (of the order of 1 °C) but post failure sliding on fractures generates large increases in temperature (greater than 100 °C in many instances). This work suggests that although the initial generation of fracture surfaces is weakly exothermic (mode 1 cracking is weakly endothermic), the gross stages of fracturing involving sliding are strongly exothermic. Similar results follow from the work of Brantut et al. (2011, 2008) and Togo and Shimamoto (2012). The same conclusions follow from considerations of the heat generated during sliding on large faults (Rempel and Rice, 2006; Rice, 2006). The conclusion from this work is that relatively little energy is dissipated in grain or rock breakage; most energy is dissipated as heat during subsequent sliding on surfaces. The subject is still quite open and considerable new work (both experimental and theoretical) is warranted.

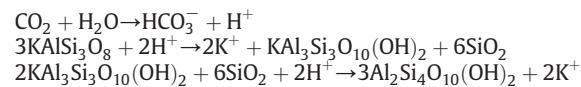
3. Hydrothermal mineralising systems as open flow chemical reactors

Although there is a huge literature associated with hydrothermal systems in convergent plate tectonic settings (see discussion by Robb (2005), and references therein) there is an increasing awareness that many very large mineralised hydrothermal systems have formed in intracratonic settings, far removed (say 300–500 km) from subduction zones (Begg et al., 2009). In either case there are sources of fluids at some depth that are thought to be important for the development of the mineralising system. In the case of systems directly associated with subduction the fluids presumably arise from dehydration of the subducting slab and/or from crystallising melts that either originate at the subducting slab or are derived from melting of material above the subducting slab. In the case of intracratonic systems associated with old cratonic margins, the proposal is that the fluids arise from devolatilisation and/or melting of old metasomatised sub-continental lithosphere in a tectonic event subsequent to formation of the old margin (Begg et al., 2009; Gorczyk et al., 2012). In addition some mineralising systems may be formed totally or in part from shallow crustal or meteoric fluids that are driven by gradients in hydraulic potential arising from topographic relief. Specifically, in IOCG deposit models a source of saline fluids from evaporitic sequences is postulated

(Haynes et al., 1995) although mechanisms for driving the flow of these fluids are not well defined. In each case there is a source of fluids that supplies dissolved chemical species and heat to the mineralising system over an extended (but geologically short) period of time so that the systems operate as open flow systems (Figs. 3.1, 4.1c, d). In the case of systems formed deep in the crust the fluid pressure gradient is at or close to lithostatic and the systems are flow controlled. For systems formed close to the surface of the Earth the fluid pressure gradient is close to hydrostatic and the systems are hydraulic-potential controlled. Other environments, particularly those controlled by magmatic activity, involve flow controlled by fluid pressure, and/or fluid convection may be involved. These various types of open flow systems are discussed in Section 4.1.

Hydrothermal ore systems provide a clear example of non-equilibrium phenomena in the geosciences (Henley and Berger, 2000). These systems commonly consist of a volume of highly mineralised, heterogeneous rock enclosed within a capsule of un-mineralised but strongly altered rock and are characterised by the following features, all of which are hall-marks of non-equilibrium systems:

- Large spatial gradients in the concentrations of chemical components expressed as mineralogical patterning and zoning at a wide range of spatial scales within the mineralised system (Berger and Henley, 2011; Henley and Berger, 2000, 2011). An example is the Witwatersrand gold/uranium hydrothermal system (Barnicoat et al., 1997; Jolley et al., 1999, 2004) where regional scale alteration of quartz-K-feldspar bearing rocks by H⁺ metasomatism forms assemblages of pyrophyllite, muscovite, chlorite, chloritoid and kaolinite (Fig. 3.2). The reactions:



are relevant (Barnicoat et al., 1997). Barnicoat et al. (1997) suggest that the third exothermic reaction consumes quartz and hence supplies a possible chemical mechanism for generating or maintaining permeability during fluid flow and alteration. Zhao et al. (2009) model these reactions and show a marginal increase in porosity during the reaction, enough however to maintain any imposed flow. The mineralisation stage in the Witwatersrand is associated with a decrease in temperature and associated widespread fracturing in competent units (silicified conglomerates) with the deposition, *inter alia*, of uraninite, gold and carbon within the fractures. Notice that the system of equations above, in common with many alteration systems, is driven by the supply of H⁺.

- A patterned distribution of mineralogy both inside and outside the ore body. The alteration envelope is commonly very large (tens of cubic kilometres or larger) compared to the mineralised parts of the system. Examples are given by Dube and Goselin (2007), Eastoe et al. (1987), Large et al. (2001), and Muntean et al. (2011). An important avenue of investigation is to explore if there are hitherto unrecognised structures or patterns within such an envelope that might act as vectors towards mineralisation.
- A tendency for mineralisation to be localised at or near the site of large gradients in pH and Eh; this spatial association with gradients in Eh and pH can be fractal (or at least power-law) in its spatial distribution in that the association occurs at the scale of hundreds of kilometres through to nano-metre scales. Such power-law distributions are characteristic of critical systems (Sornette, 2000). An example is shown in Fig. 3.3 from the Yilgarn gold deposits of Western Australia. This shows the association of gold deposits with gradients in arsenic concentration from the regional-scale (Fig. 3.3a) to the grain-scale (Fig. 3.3b) to the nano-scale (Fig. 3.3c); this represents a scale invariant association of gold with arsenic gradients over a range of $\approx 10^{15}$! Similar associations with gradients in pH and/or Eh

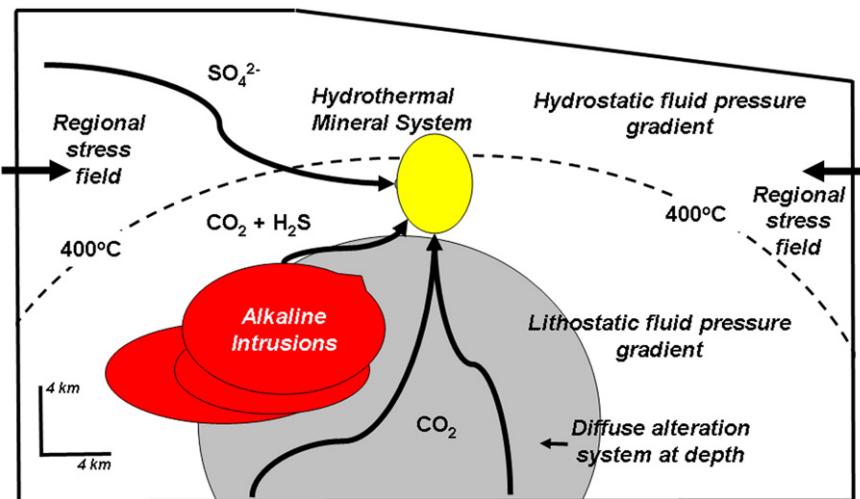


Fig. 3.1. A conceptual model of an open flow hydrothermal system.

are documented by Neumayr et al. (2005, 2008), Phillips (1986) and Prendergast (2007).

- An apparently irregular distribution of mineralisation within the ore body that is reflected as a multi-fractal distribution of mineralisation (Arias et al., 2011; Bastrakov et al., 2007; Ford and Blenkinsop, 2009; Hunt et al., 2007; Li et al., 2009; Oreskes and Einaudi, 1990; Qingfei et al., 2008; Riedi, 1998; Sanderson et al., 2008). Fractal (or at least, power law) distributions of mineralisation are reported by Carlson (1991) and Schodde and Hronsky (2006).
- The mineralisation phase is commonly associated with or post-dates fracturing, veining, stockwork formation or brecciation at various spatial scales. Examples are given by Barnicoat et al. (1997) for the Witwatersrand system, by Dube and Goselin (2007) for orogenic gold systems and by Bastrakov et al. (2007), Haynes et al. (1995), Hunt et al. (2007) and Oreskes and Einaudi (1990) for IOCG deposits including Olympic Dam. An example from the Tropicana gold deposit in Western Australia is given in Fig. 3.4. In general these “brittle-failure” events occur relatively late in the history of the system and overprint an earlier phase of regional alteration which consists of H^+ metasomatism in the case of the Witwatersrand system, carbonate

alteration in the Yilgarn orogenic gold deposits (Phillips, 1986), sericite-haematite rich assemblages in the case of Olympic Dam and magnetite alteration in the case of some deposits in the IOCG province of South Australia (Bastrakov et al., 2007). This fracturing phase, at least in some IOCG systems, is commonly associated with the formation of widespread haematite alteration (Haynes et al., 1995; Oreskes and Einaudi, 1990), in orogenic gold deposits with pyrite and pyrrhotite (Elmer et al., 2007), and in the case of the Witwatersrand system, with the precipitation of carbon-bearing phases (Barnicoat et al., 1997).

- A time sequence of minerals within the ore system defined by spatial over-printing relations; this is commonly referred to as a *paragenetic sequence*. An example from the Witwatersrand system is given in Fig. 3.5. Although the sequence fracturing-uraninite-hydrocarbon-gold is shown only once in this diagram for the Witwatersrand it is probable that this sequence was repeated several times (Barnicoat et al., 1997). In fact multiple overprinting events are reported in many deposits. Examples include multiple high/low temperature events associated with brecciation, oscillations in Eh/pH and mineralisation at Olympic Dam (Haynes et al., 1995) and in epithermal gold deposits (Berger and Henley, 2011; Henley and Berger, 2011).

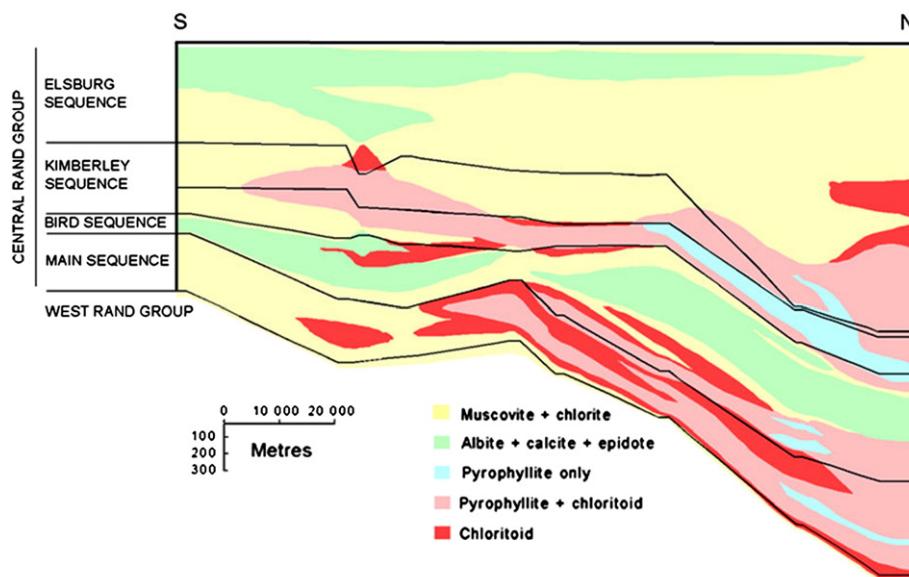


Fig. 3.2. Alteration associated with the Witwatersrand hydrothermal system.

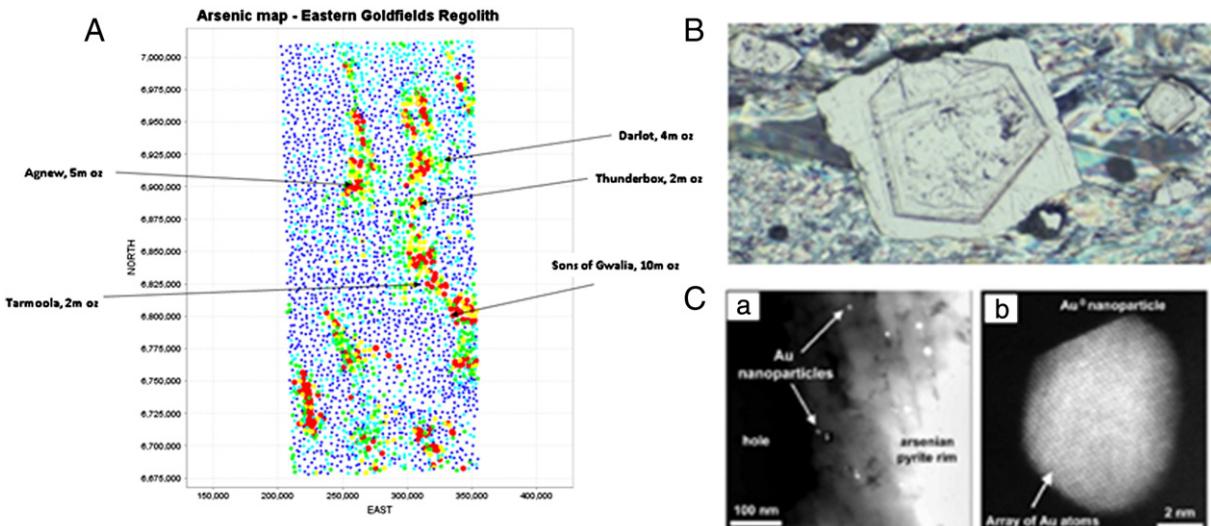


Fig. 3.3. Spatial invariance of gold associated with gradients in arsenic concentration in the Yilgarn gold deposits of Western Australia. (A) Regional scale (supplied by Scott Halley). (B) Grain-scale (photo by Brett Davis; supplied by Scott Halley). (C) Nano-scale (from Reich et al., 2005).

- The observation that although ore bodies can be grouped into categories such as epithermal, MVT, IOCG, or orogenic gold, all ore bodies are different thus suggesting a strong dependence on initial conditions. This is brought out for instance in the spectrum of ore body types within in the IOCG class suggested by Bastrakov et al. (2007) and Hunt et al. (2007).

Although many studies, based on the local equilibrium assumption and associated with the deposits mentioned above, enable the mineral assemblages to be reproduced and the gross features of the mineral paragenesis to be understood, the studies in general fail to explain why the particular deposit is large or small, why brecciation or (stockwork) veining is an integral part of the evolution of the system controlling the localisation of mineralisation and why the paragenesis, fracturing and sometimes the temperature and Eh/pH may oscillate through many episodes. In many of the cases resort is made to fluid mixing scenarios which successfully explain the mineralogy of the system and aspects of the paragenesis. As mentioned such scenarios are invariably based on the assumption of local equilibrium and hence by definition neglect any processes responsible for the evolution of the system. The progressive development of any system has to be based on an understanding of the processes involved in the evolution of the system and hence depends on a non-equilibrium approach. This is the topic of the next section.

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, ΔG , is a Lyapunov function for closed systems and drives the reactions to equilibrium; the excess work, Γ , defined by Ross (2008) for the reaction $A \rightarrow X \rightarrow B$ as

$$\Gamma = \int_{n_X^{\text{ss}}}^{n_X} (\mu_X - \mu_X^{\text{ss}}) dn_X \quad (3.1)$$

is a Lyapunov function for both closed and open systems that drives the reactions to a stationary state. μ_X , μ_X^{ss} and n_X , n_X^{ss} are the chemical potentials and numbers of moles of X at an arbitrary non-equilibrium state and at a stationary state respectively. This reaction continues at the stationary state until all of A is consumed when the reaction stops; it never reaches equilibrium yet the product is characterised by the value of μ_X^{ss} . Γ is a state function and is an extremum at all steady states; $\Gamma \geq 0$ for a

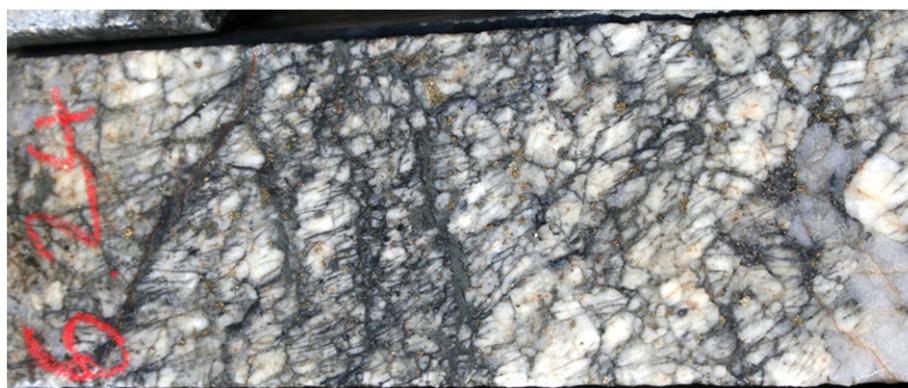


Fig. 3.4. Brecciated diamond drill core from the Tropicana gold deposit in eastern Western Australia. Biotite selvages and pyrite characterise the alteration mineral assemblages. The gold grade in this part of the core is 6.24 g t^{-1} . Diameter of core is 48 mm.

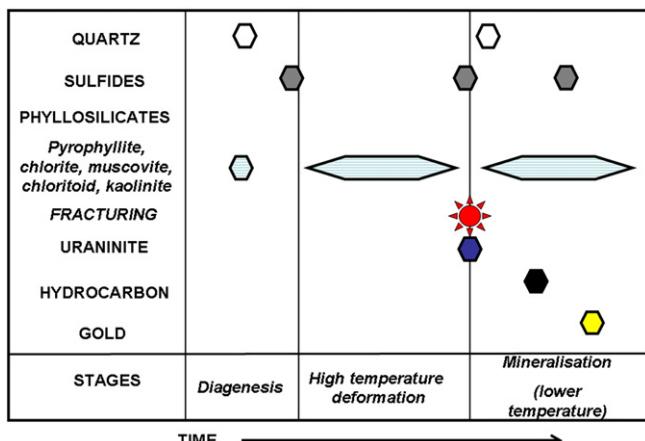


Fig. 3.5. Example of a paragenetic sequence from the Witwatersrand hydrothermal system.
Modified after Barnicoat et al. (1997).

displacement from a stationary state. The equivalent statements for 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 work 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 steady 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; Landsberg, 1961). The phase rule is simply a statement of 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 at or far from equilibrium depending on the constraints

on M and r_k ; $\sum_{n=1}^k r_n = 1$. f is the number of independent intensive variables. 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 (Callen, 1960). If there are R independent chemical reactions the phase rule becomes $f = r - M - R + 2$ (Kondepudi and Prigogine, 1998, p 182). Korzhinskii (1966, 1967) points out that for open flow systems there is a set of chemical components (called by Korzhinskii, mobile components) where the chemical potentials are fixed outside of the control volume. This reduces the number of independent chemical potentials and hence reduces f so that the resulting mineral assemblages tend to be simpler than those developing in closed metamorphic systems at equilibrium. The arguments of both Korzhinskii and Landsberg 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 work (Ross, 2008) 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 in a closed system. These results are a statement of the observation that equilibrium systems are defined by states of maximum entropy (the greatest number of degrees of freedom) rather than open flow systems and closed systems at a stationary state where the entropy is constrained. All however are characterised by an ordered assemblage of mineral phases.

4. Thermodynamics, equilibrium, steady states and nonlinear chemical systems

4.1. Equilibrium and non-equilibrium states

Most treatments of metasomatism and mineralising processes adopt the concept introduced by Korzhinskii (1950) of *mosaic equilibrium* which has come to be known in the geological literature as *local equilibrium* (Thompson, 1959, 1970). The proposal is that even though the system is manifestly not at equilibrium one can identify a large-enough region for the system that can be considered to be at equilibrium. The evolution of the system can then be built up by considering the interactions between these regions. The notion of equilibrium is pervasive in metamorphic and metasomatic petrology, to the extent that the concept is commonly treated as self evident for most geological systems. By definition however, systems are not at equilibrium during their evolution and there are many situations, which we will discuss, where even the smallest region, in which concepts such as temperature and internal energy can be defined by some kind of averaging of molecular motions, is not at equilibrium.

It is convenient in what follows to retain the concepts of extensive and intensive variables inherited from equilibrium thermodynamics. We use f_k as the set of additive quantities such as volume and entropy, known as *extensive variables*. The sets of quantities, λ_k , are *non-additive* quantities such as pressure and temperature and are known as *intensive variables*. In systems far from equilibrium these quantities are defined at each point in the system and vary from one point to another. In systems at equilibrium these quantities have the same value at each point in the system.

Four types of thermodynamic systems are distinguished (Niven, 2009; Niven and Andresen, 2010). The first is an *isolated system* where extensive variables such as the internal energy, u , the volume, V , and the number of moles of k chemical components, n_k , are kept constant. The system is isolated from other systems by an impermeable wall (Fig. 4.1a). 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 Gibbs energy or by maximising an entropy function. The number of mineral phases that can coexist is defined by the Gibbs phase rule (Callen, 1960). 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) and elaborated upon by numerous authors including Weinhold (1975a,b,c,d, 1976); for a review see Niven and Andresen (2010). The path from one state to the equilibrium state need not necessarily be steady. We will see in Section 6 that in an isolated system even a simple exothermic reaction of the type $A \rightarrow B$ can produce oscillations in the concentration of B and in the temperature (Gray and Scott, 1990) as the system proceeds to equilibrium. Nevertheless, an isolated system must ultimately proceed smoothly to equilibrium as far as functions such as the Gibbs energy are concerned. In fact ΔG is a function which is important far from equilibrium even though the property $\Delta G = 0$ is the emphasis in equilibrium thermodynamics. As indicated in Section 3, ΔG is always ≤ 0 , is a function that can be defined at or far from equilibrium and has the property that it proceeds smoothly to a stationary state, namely, equilibrium for systems at constant temperature and pressure; such functions are known as Lyapunov functions (Ross, 2008, see Section 8).

The second type of system, a *diffusive system* (Fig. 4.1b), is also known as a *closed system*. The system is embedded in another medium which acts as a *bath* and which itself is isolated from all other systems by an impermeable wall. Intensive variables such as T and P are held constant in the bath and the diffusive system can interact with the bath by interchange of mass, n_k , and heat. Diffusive systems must always evolve to equilibrium and follow the same rules for doing so as do isolated systems. Clearly most considerations of metamorphic mineral reactions assume that the system is isolated or

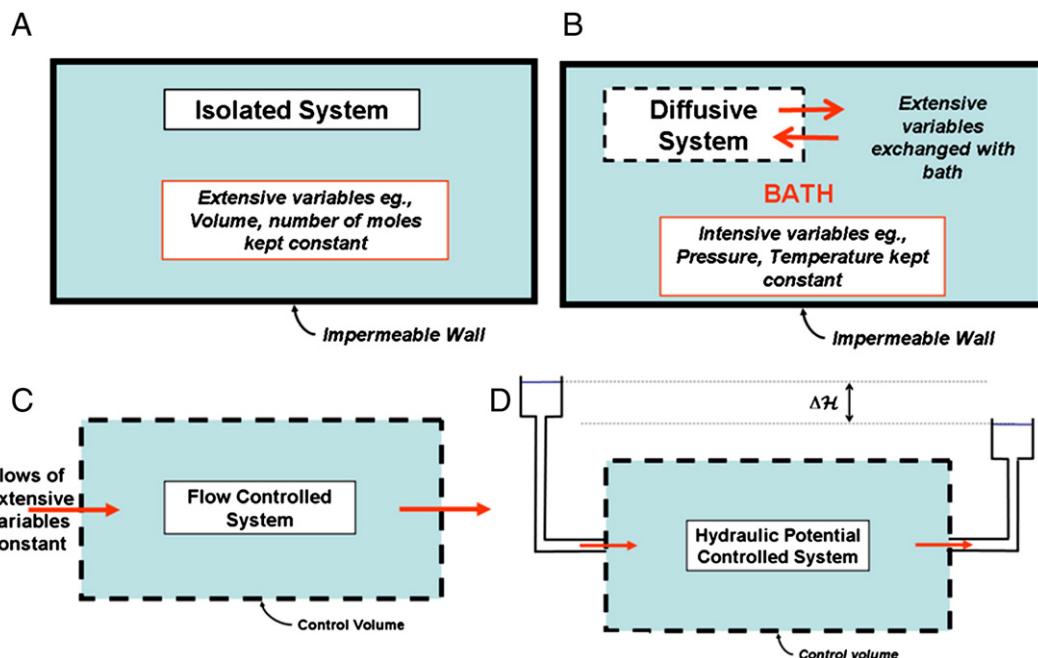


Fig. 4.1. Types of thermodynamic systems. (A) Isolated system. Extensive variables are kept constant. The system is isolated from any other system. (B) Diffusive system. The system can communicate with the surrounding bath where intensive variables are kept constant. The bath is isolated from any other system. (C) Flow-controlled system where flows of extensive variables are kept constant within a region known as the control volume. (D) Hydraulic potential control system where the flows of extensive variables are controlled by a gradient in hydraulic potential. 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.

diffusive although the distinction is not commonly well defined or emphasised. The mineral phases that can coexist in both isolated and diffusive systems for extended periods of time at non-equilibrium stationary states are defined by a phase rule where the chemical potentials of the k chemical components are held at stationary state values as defined by the Ross excess work concept (Ross, 2008). This in general means that the number of co-existing phases is less than in the final equilibrium state.

A completely different class of systems are those called *open flow* systems (Figs. 4.1c, d) where the system comprises an open configuration that can communicate with the surrounding material with or without constraints on the flow of mass and heat through the system. One of these systems, the third type of system, is an *open flow controlled* system (Fig. 4.1c) and is the type of relevance to mineralising systems where the fluid input rate is constrained by the rate of production of the fluid (Phillips, 1991, pp 135–139). This we propose is the case for orogenic gold deposits and IOCG deposits. The region of interest through which flow systems operate is known as a *control volume* (Niven, 2009). The boundaries of the control volume may be either permeable or impermeable and may be fixed spatially or migrate with time. Nevertheless it is always fundamental to define the control volume in order to be precise in discussing the evolution of the system. It is important to note that if the flow rate is held constant the initial porosity and permeability of the system, in general, need to adjust to new values by mechanical and/or chemical means to accommodate the imposed flow as the system evolves (Section 5). 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. Such systems evolve to a non-equilibrium stationary state so long as the flows are maintained and the system can be held far from equilibrium for the duration of the flows. Systems with episodic or punctuated flow are clearly important in hydrothermal systems (Cox, 1995; Cox and Ruming, 2004; Miller and Nur, 2000; Sibson, 1987, 1992) but we concentrate on steady flows in Part I in order to establish the principles involved. Unsteady flow is considered in Part II.

If F_k^{in} is the volumetric flow of f_k into, and F_k^{out} the volumetric flow of f_k out of the system, and if \dot{f}_k^{prod} is the rate of production of f_k inside the system, then the net rate of production of f_k is

$$\frac{df_k}{dt} = (F_k^{in} - F_k^{out}) + \dot{f}_k^{prod} \quad (4.1)$$

which is similar to Eq. (2.9).

For a stationary state $\frac{df_k}{dt} = 0$ and so

$$\dot{f}_k^{prod} = F_k^{out} - F_k^{in} \quad (4.2)$$

Eqs. (4.1) and (4.2) are used extensively in Section 6 to discuss the behaviour of various types of chemical reactions in flow controlled systems and have been used by Gray and Scott (1990) to produce *flow diagrams* which are powerful and convenient graphic representations of the stationary states of chemical reactions in flow controlled systems.

The fourth type of system, a *hydraulic potential controlled* flow system (Fig. 4.1d) is similar to a flow controlled system except that the volumetric flow rate is imposed by a gradient in the hydraulic potential. 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 system changes as the permeability within the system changes due to chemical precipitation and/or dissolution. The thermodynamics of such permeability evolution is considered by Coussy (1995). In order to achieve a stationary state the rates of chemical precipitation and/or dissolution must evolve in order to satisfy $\frac{\partial(\phi c_i)}{\partial t} = 0$. These kinds of systems are typical of MVT and Irish lead/zinc deposits as well as uranium unconformity deposits (Anderson and Garven, 1987; Appold and Garven, 2000; Appold et al., 2007; Garven, 1985; Garven and Freeze, 1984a, 1984b; Murphy et al., 2008; Raffensperger and Garven, 1995a, 1995b). These types of systems essentially close down if the permeability becomes very

low due to mineral precipitation and if there is no driver in the system to increase the permeability by mechanical or chemical means.

Note that for flow systems, flow controlled systems with constant input flow correspond to Neumann boundary conditions (where the derivatives of the fluid pressure are fixed at the boundaries) whereas hydraulic potential controlled flow systems correspond to Dirichlet boundary conditions (where the values of the fluid pressure are fixed at the boundaries). It is of course possible to have mixed (Robin) boundary conditions. These may be relevant to situations such as are shown in Fig. 1.1(A). The mineral phases that can coexist at steady state are defined by the Ross excess work concept (Ross, 2008). The results are similar to those that result from the Korzhinskii (1950, 1965, 1966, 1967) discussions of the application of the phase rule concept to open systems (see Section 3).

Over the past 80 years or so, four major lines of thought regarding systems not at equilibrium have developed. These are all compatible (except for some important details) and are converging on a common treatment of nonlinear systems not at equilibrium. These lines of development are summarised below:

- (a) Onsager (1931a,b) and Onsager and Machlup (1953) developed a thermodynamically linear theory of non-equilibrium systems with the intent that such systems are 'close' to equilibrium. The treatment was elaborated upon by de Groot and Mazur (1984) and Prigogine (1955) to encompass mainly chemical systems. By *thermodynamically linear* is meant that the *thermodynamic forces* such as gradients in chemical potential, deformation and temperature are linear functions of the *thermodynamic fluxes* such as chemical diffusive flux, momentum flux (per unit area) and heat flux respectively. The Onsager approach is widely used but Ross and co-workers (Hunt et al., 1987, 1988; Ross, 2008; Ross and Villaverde, 2010; Ross and Vlad, 2005; Ross et al., 1988; Villaverde et al., 2011) have pointed out that for *any* isolated or diffusive chemical system (even the simplest and no matter how close to equilibrium) the chemical affinity is *never* a linear function of the chemical reaction rate (Ross, 2008) so that Onsager principles are never applicable to chemical reactions no matter how close the system is to equilibrium. These references also discuss what is meant by the terms *close to* and *far from* equilibrium.
- (b) The application of thermodynamics to deforming reacting systems was developed from a non-Onsager (that is, nonlinear) point of view by Truesdell (1966a,b) based on work by Coleman and Noll (1963). This involved the definition of state functions which in turn are functionals of *internal* variables that define the non-equilibrium state of the system; a functional is a function of a function (Truesdell, 1966a). Somewhat similar strands of this development were initiated by Biot (1955, 1984) who introduced the concept of the Helmholtz energy for a stressed solid. That strand was further developed by Collins and Housby (1997), Collins and Hilder (2002), Coussy (1995, 2004, 2010), Housby and Puzrin (2006), Kestin and Rice (1970), Rice (1971) and Ziegler (1963). This approach is now commonly known as *Generalised Thermodynamics* (Hobbs et al., 2011). We elaborate on these concepts in Section 4.1.1.
- (c) A completely different line of activity developed independently of the above approaches and independently of each other in nonlinear chemistry and chemical engineering but with parallel activity in biology. The concepts involve isolated, diffusive and flow controlled systems and are based on determining the stationary states for chemical reactions that are coupled. The term *coupled* means that the concentration of a particular component is produced or consumed in more than one reaction (as proposed by Carmichael, 1969 for metamorphic reactions) and/or feedback mechanisms exist for the rate of production of that component as a result of thermal effects, flow (in the form of

diffusion and fluid advection) or deformation. Both coupling and feedback commonly lead to multiple stationary states and the procedure then is to establish which states are stable or unstable. A state is said to be stable if a small perturbation from that state results in the system returning to that state. Unstable states are those where the perturbation continues to grow so that the system moves to another state. The stationary states are further analysed using methods well established in nonlinear dynamics (Cross and Greenside, 2009; Epstein and Pojman, 1998; Gray and Scott, 1990; Guckenheimer and Holmes, 1986; Wiggins, 2003) to describe the details of the path or paths the system will follow once perturbed (by a small or large amount). A diverse range of behaviours is possible including oscillatory behaviour in both space or time, travelling compositional waves and chaotic behaviour both in space and time (Epstein and Pojman, 1998; Gray and Scott, 1990; Murray, 1989; Ortoleva et al., 1987a, 1987b; Prigogine, 1955; Ross, 2008; Scott, 1994; Turing, 1952). These processes are fundamental for understanding mineralising systems both from the point of view of spatial pattern formation (compositional zoning, pH and redox fronts) and of temporal oscillatory behaviour (oscillations in temperature, redox and pH in time at a given place in the mineralising systems). These issues are considered in detail in Section 6.

- (d) The fourth approach derives largely from the work of Jaynes (1963, 2003) and although its basis is in the statistical physics of systems at equilibrium it has evolved into general thermodynamic arguments (Niven, 2009, 2010b; Niven and Andresen, 2010). The approach is characterised by the search for extrema (both minima and maxima) in functions (or functionals) that represent the entropy or the entropy production or that represent some measure of the energy or of the energy dissipation. The correspondence in principle with the search for extrema in the entropy or the Gibbs energy in classical equilibrium thermodynamics (Callen, 1960; Gibbs, 1906) is clear. In equilibrium thermodynamics the use of extremum principles is to predict the *equilibrium state* under constraints imposed by intensive or extensive variables. In non-equilibrium thermodynamics the use of extremum principles is to predict the *stationary states* of a flow system under constraints imposed by thermodynamic fluxes or thermodynamics forces. For details see Niven (2009, 2010a) and Niven and Andresen (2010). The great potential of this approach is that it will reveal some general rules for how nonlinear systems evolve with time without investigating all the details of the individual processes involved in the evolution. For mineralising systems, for which a great range of interacting chemical species and mechanical behaviours are postulated, this is particularly relevant. The approach at present for mineralising systems is to add more and more detail to models of mineralising systems in an attempt to reproduce and couple all of the processes in Fig. 1.2. The result is that one is forced to make simplifying assumptions such as local equilibrium or a lack of coupling between mechanical–thermal–chemical–fluid processes in order to examine models that are tractable on large, modern computers. The situation has its parallel in modern general circulation models of the climate of the Earth where more and more detailed mechanisms with associated feedback effects are incorporated into the models. The spectacular successes of extrema methods in this case are the results of Paltridge and others (Niven, 2009; Ozawa and Ohmura, 1997; Ozawa et al., 2003; Paltridge, 1975, 1978, 1981, 2001; Paltridge et al., 2007; Shimokawa and Ozawa, 2001, 2002) who reproduce details of the Earth's climate including detailed distributions of temperature and cloud cover with a very simple model and the assumption that the entropy production for the system is a maximum. A similar goal for describing the evolution of

mineralising systems with the bare minimum of detail and some extremum principle should be the goal of future work. We elaborate upon these concepts in Sections 4.1.2 and 8.

4.1.1. Generalised thermodynamics

The approach known as *Generalised Thermodynamics* (Houlsby and Puzrin, 2006; Collins and Hilder, 2002) is the obvious generalisation of classical equilibrium thermodynamics to the study of deforming-chemically reacting-hydrodynamic-thermal systems not at equilibrium; this subject adopts a different approach to that of assuming local equilibrium. Generalised thermodynamics is based on the proposition (arising from Biot, 1954) that the specific Helmholtz energy, Ψ , which varies with position, \mathbf{x} , within the system and with time, t , is defined at each point, by

$$\Psi(\mathbf{x}, t) \equiv u - Ts \quad (4.3)$$

where $u(\mathbf{x}, t)$ is the specific internal energy, $T(\mathbf{x}, t)$ is the absolute temperature, and $s(\mathbf{x}, t)$ is the specific entropy. This proposition is equivalent to assuming that the first and second laws of thermodynamics apply in all non-equilibrium situations and that in any system the first law can be written as: *At each point in any system the concept of internal energy exists and the internal energy can be defined in terms of quantities (state variables) that describe the state of the system*. The assumption also involves a statement of the second law as: *At each point in any system the concepts of entropy and temperature exist and the entropy production is always greater than zero except at equilibrium*. Such propositions are based on day to day experience (Truesdell, 1966a, 1966b) but assume that there exists a region associated with the system, small (perhaps of the order of nano-metres) compared to length scales (such as sub-grain size) but large enough that the concepts of internal energy, entropy and absolute temperature have meaning as some kind of time- and space-averaged quantities. This implies a time scale for definition of these quantities (perhaps of the order of nano-seconds) that is large compared to the time-scales associated with thermal vibration of molecules and small compared to the rates of other processes in the system such as deformation, fluid flow and chemical reactions. The small region is meant to be a thermodynamic continuum. The position vector, \mathbf{x} , is defined with respect to a convenient set of coordinate axes and defines the centre of mass of the small region. From a macroscopic point of view Ψ may then be considered a continuous function of position. Once the entropy, s , is defined at each point the temperature is related to Ψ by $T = -\frac{\partial\Psi}{\partial s}$. The proposition that Ψ can be defined for a stressed, plastically deforming, chemically reacting material was introduced by Biot (1954) and has been progressively refined by Biot (1984), Coussy (1995, 2010), Houlsby and Puzrin (2006), Rice (1971), and Truesdell (1966a,b). The Gibbs energy is then defined (Rice, 1971) as the Legendre transform of Ψ . For a recent discussion of the Gibbs energy in deforming elastic-plastic solids see Plohr (2011).

In addition to Eq. (4.3), Ψ may be written (Coussy, 2004; Houlsby and Puzrin, 2006; Kestin and Rice, 1970; Truesdell, 1966a, 1966b) as an expression of the form

$$\Psi \equiv u - Ts = \Psi(\varepsilon_{ij}^e, \varepsilon_{ij}^p, T, \nabla T, \mu^K, \nabla \mu^K, \dots) \quad (4.4)$$

where ε_{ij}^e is the elastic strain tensor, ε_{ij}^p is the plastic strain tensor, ∇T is the temperature gradient, μ^K is the chemical potential of the K th chemical component and $\nabla \mu^K$ is the gradient in this chemical potential. The quantities inside the brackets in Eq. (4.4) are known as *state variables*; they define the non-equilibrium state of the system no matter how far from equilibrium the system may be. As the system approaches equilibrium these state variables approach the classical equilibrium state variables.

In some literature (Fitts, 1962; Prigogine, 1955; Ross, 2008) concerning systems not at equilibrium, an assumption of this type is called the *assumption of local equilibrium*. This usage is conceptually

quite different to that employed by metamorphic and metasomatic geologists. The nominated small region may be undergoing plastic deformation, gradients in temperature and chemical potential may exist and Ψ may be changing with time, so there is no requirement from Eq. (4.4) that this small region be at equilibrium as pointed out by Fitts (1962). Hence we prefer the term *assumption of local state* due to Coussy (2004, p 48). The fundamental postulate is that Ψ can be defined at each "point" in the system no matter how far the system is from equilibrium and is a varying function of both position and of time. We reserve the phrase *assumption of local equilibrium* for that state commonly referred to by metamorphic and metasomatic petrologists (Korzhinskii, 1950; Thompson, 1959, 1970) to mean the *largest* region in the system that can be considered to be at equilibrium. Throughout such a region an assumption of local equilibrium proposes that there are no gradients in the state variables and that Ψ is independent of time and is spatially homogeneous.

In addition to Ψ , another functional, the dissipation functional, Φ (which is a scalar quantity), is required to define the evolution of any system not at equilibrium (Biot, 1984; Collins and Houlsby, 1997; Houlsby and Puzrin, 2006). The dissipation functional is defined by $\Phi \equiv T\dot{s}$ so that it expresses the entropy production at a given temperature. By the second law of thermodynamics $\Phi \geq 0$, and $\Phi = 0$ at equilibrium. If there are R different processes operating in a system then

$$\Phi = \sum_{k=1}^R \Phi^k \geq 0.$$

Generalised thermodynamics is the framework that one would use to develop a detailed model of hydrothermal systems that incorporates all of the individual processes involved in the evolution of the system and ensures that the framework is thermodynamically admissible (is consistent with the first and second laws of thermodynamics). Although this is a relevant and undoubtedly revealing pursuit another approach is to develop generalised models with the minimum of detail but that still reveal the critical controls on the evolution of the hydrothermal system. This latter approach involves the use of extrema principles in thermodynamics.

4.1.2. Extrema thermodynamic principles

There is a long history in the use of extrema principles in thermodynamics not the least of which are the minimisation of the Gibbs energy and the maximisation of entropy developed and used by Gibbs (1873, 1875–1878) for systems at equilibrium. Similar principles were developed for non-equilibrium systems and a review is given by Niven and Andresen (2010). These principles are based on finding extrema for the entropy production. To be clear the quantity *entropy production* describes the *rate* at which entropy is produced in a system and has units of $J K^{-1} s^{-1}$. The specific entropy production has units of $J kg^{-1} K^{-1} s^{-1}$.

The well known non-equilibrium extrema principles are those of Prigogine (1955) who proposed a *minimum entropy production principle* and of Ziegler (1963) who proposed a *maximum entropy production (MEP) principle*. Although these two principles appear to be contradictory they are conceptually quite different (Niven and Andresen, 2010; Ziegler, 1963). Detailed criticism of the Prigogine principle is given by Hunt et al. (1987, 1988), Ross (2008), Ross and Villaverde (2010), and Ross and Vlad (2005). It is to be noted that the concept does not appear in some recent textbooks on chemical thermodynamics (Kondepudi, 2008) whereas it features prominently in Kondepudi and Prigogine (1998). The Ziegler MEP principle is widely used in continuum mechanics (Coussy, 1995, 2004; Houlsby and Puzrin, 2006).

The usage of extrema principles was enhanced by the work of Jaynes (1957, 1963) based on statistical mechanics. For reviews and discussions of this approach see Niven and Andresen (2010). We will not discuss the detailed theory here but point to some developments that are relevant to understanding hydrothermal systems viewed as open flow reactors.

One development from the initial Jaynes approach is *finite time thermodynamics* developed by workers such as Salamon and

Andresen (Andresen and Gordon, 1994; Crooks, 2007; Nulton et al., 1985; Salamon and Berry, 1983; Salamon et al., 1980). Finite time thermodynamics uses minimum entropy production principles to calculate the fundamental limit of efficiency of a process in which a thermodynamic system is moved from one equilibrium position to another along a specified path at specified rates. The geodesic (shortest path) defined for the entropy production manifold (the surface defined by all the entropy production states) is used to determine the most efficient path. The method has been generalised for open flow systems as they move from one steady state to another (Niven and Andresen, 2010) and this generalisation has the potential to be of great use in future theories of hydrothermal systems.

Further developments of the Jaynes approach particularly to flow controlled systems have been made by Niven (2010b). The hypothesis is that many dynamical flow systems evolve to arrive at a steady state that achieves maximum entropy production rather than maximum entropy production being a result of the detailed dynamics of the system. This applies to systems close and far from equilibrium, is applicable to both thermodynamic linear and nonlinear systems and to systems where multiple coupled processes operate. Dissipative flow systems move to a steady state defined by minimisation of a generalised energy functional for each fluid element. This corresponds to a state of maximum entropy production rate for each fluid element (Niven, 2009). The system is constrained by the mean fluxes. Flow systems are driven to states that represent maximum disequilibrium; see §1 p 10 of Niven (2009).

A slightly different approach has been taken by Bejan (2007, 2006) who uses minimum entropy production principles to produce the most efficient design of chemical reactors. He concludes that: *For a finite sized flow system to persist in time it must evolve in such a way that it provides easier and easier access to the currents that flow through it.*

One of the most instructive applications of extrema principles to flow controlled systems is that of Niven (2010b) for flow in single and two (parallel) pipe systems. He shows that for a single pipe the Ziegler MEP principle can be used as a selection criterion for the transition from laminar to turbulent flow in the system. For a constant flow 2-pipe system a minimum entropy production principle can be used to define the stationary state for a given imposed flow and the Ziegler MEP principle still defines the transition from laminar to turbulent flow. For a 2-pipe system with a constant hydraulic potential as the boundary condition the selection of flow regimes is based on a minimum entropy production principle whereas the definition of stationary states is based on a maximum entropy production principle (different to that of Ziegler, 1963). Results such as these offer the potential that similar selection rules could be developed for hydrothermal systems whereby a maximum entropy production principle may select between different modes of operation of the system (for instance – mineralised versus un-mineralised) whereas some other form of an entropy production principle may define stationary states in each operating mode of the system. We return to this theme in Sections 6.5 and 8.

4.2. Stationary states

It is convenient in developing models for the behaviour of mineralising systems to define the conditions under which the system is in a stationary state. We repeat: *a stationary state is one where the rate of change of the mean of a particular quantity of interest is zero.* Thus for any chemical system one possible stationary state is an equilibrium state where all chemical reactions have ceased and hence the rate of change of chemical concentrations is zero. As an example consider an isothermal chemical reaction in an isolated system of the type



with a rate constant k and a reaction rate, $\dot{\xi}$, given in terms of the concentrations of A and B, a and b , by

$$\dot{\xi} = -\frac{da}{dt} = \frac{db}{dt} = ka. \quad (4.6)$$

In Eq. (4.6) the over-dot denotes differentiation with respect to time. It follows that

$$a = a_0 \exp(-kt) \text{ and } b = b_0[1 - \exp(-kt)] \quad (4.7)$$

where a_0 and b_0 are the initial concentrations of A and B. We define the extent of the reaction by

$$\xi = \frac{a_0 - a}{a_0} \quad (4.8)$$

ξ varies from zero at the start of a reaction to one at completion. The evolution of the reaction rate and the concentration are shown in Fig. 4.2. Since $a_0 + b_0 = a + b$, $\dot{\xi} = \frac{a_0 - a}{a_0} = \frac{b - b_0}{a_0}$. One can see that after a period of time the rate of change of both a and b approaches zero. Thus the system approaches a stationary state for the system but it is an equilibrium stationary state. In an isolated system this is the only stationary state for a reaction of the type Eq. (4.5); however for an open flow system, where A is continuously input, another possibility exists (Fig. 4.2c) which is considered in Section 4.3.

4.3. Linear and nonlinear chemical systems

In Fig. 4.2(a) the straight line labelled $n=1$ corresponds to reaction (4.5); such a reaction is known as a first order reaction. The curves labelled $n=0.5$ and $n=2$ correspond to the reactions $0.5A \rightarrow B$ and $2A \rightarrow B$ respectively (known as "half" order and second order reactions). Only the curve for $n=1$ represents linear kinetics. The other two involve nonlinear kinetics. All three curves approach zero monotonically at $\xi=1$. Provided the system is able to evolve towards equilibrium a smooth ultimate approach towards zero reaction rate at $\xi=1$ is true for all chemical reactions whether they take place in isolated, diffusive or open flow systems or whether the reaction has had a stable or unstable history. However we are more interested in this paper in chemical reactions where the reaction rate does not always approach zero at $\xi=1$ in a monotonic manner. Such reactions are discussed in some detail in Section 6.

The use of the term *nonlinear* needs clarification. All chemical reactions (including Eq. (4.5)) are *thermodynamically nonlinear* (Ross, 2008) in the sense that the thermodynamic force that drives the reaction (the affinity of the reaction, \mathcal{A}) is not a linear function of the thermodynamic flux (the rate of the reaction, $\dot{\xi}$). To see this consider the reversible reaction



where k^+ and k^- are the forward and reverse rate constants for the reaction. We write r^+ and r^- as the forward and reverse reaction rates. The affinity for the reaction is (Ross, 2008)

$$\mathcal{A} = kT \ln\left(\frac{r^+}{r^-}\right) \quad (4.10)$$

where k is Boltzman's constant, whilst the reaction rate is

$$\dot{\xi} = (r^+ - r^-)a. \quad (4.11)$$

Clearly \mathcal{A} is not a linear function of $\dot{\xi}$.

However even though a reaction such as Eq. (4.5) is thermodynamically nonlinear it still has linear reaction kinetics as shown by

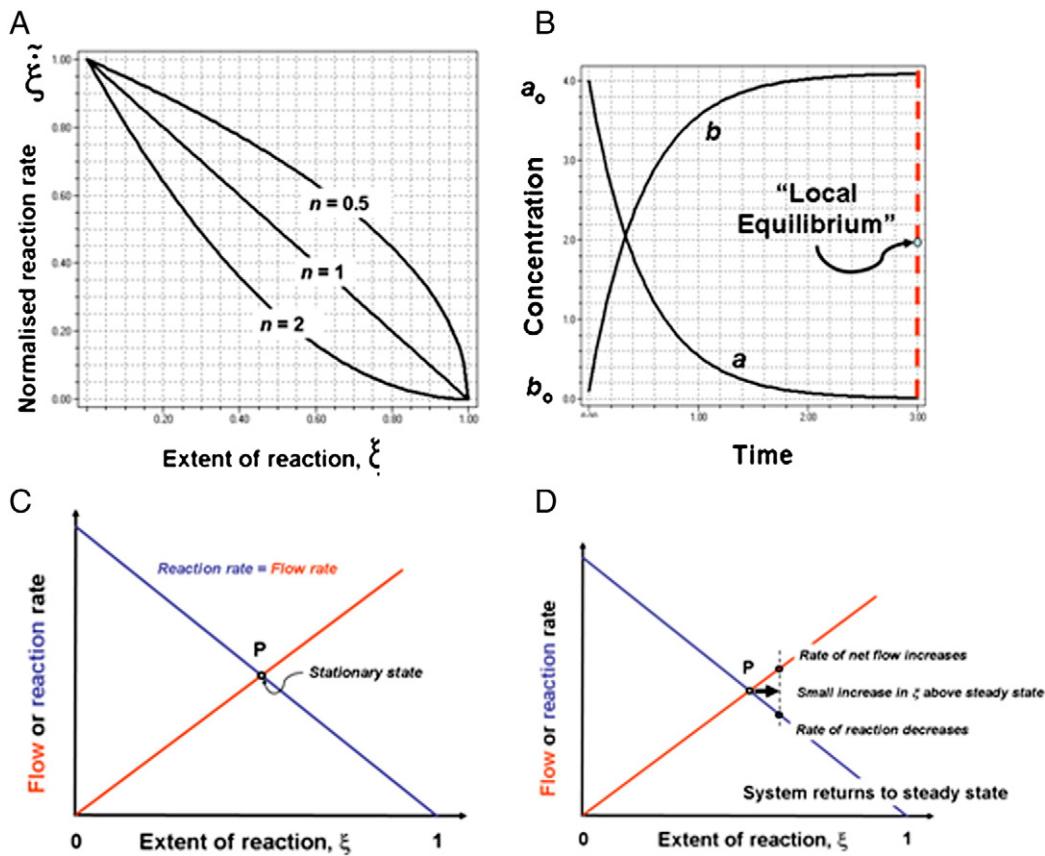


Fig. 4.2. Uncoupled kinetics. (A) Normalised reaction rate plotted against extent of reaction, ξ for the reactions $A \rightarrow B$ ($n = 1$), $0.5A \rightarrow B$ ($n = 0.5$) and $2A \rightarrow B$ ($n = 2$) in an isolated system. The reaction rate is normalised against the maximum reaction rate for each of these reactions. (B) Evolution of concentrations a and b over time for the reaction: $A \rightarrow^k B$ with initial concentrations a_0 and b_0 . After dimensionless time equal to 3 here the concentrations a and b have approached steady state and the condition of "local equilibrium" is commonly applied to such situations. (C) An open flow controlled system for a reaction with first order kinetics and the net flow rate a linear function of the reaction extent. The intersection of the net flow rate line with the reaction rate line represents a non-equilibrium stationary state. (D) A qualitative argument showing that the stationary state defined in (C) is stable. A small perturbation from the stationary state decays back to the stationary state.

Eq. (4.6) and the straight line plot corresponding to $n=1$ in Fig. 4.2(a). The plots for $n=2$ and $n=0.5$ in Fig. 4.2(a) exhibit nonlinear kinetics. In Fig. 4.3(a) we show the normalised reaction rates for what are called quadratic and cubic autocatalytic reactions and for a reaction of the form (4.5) but which is exothermic. These reactions are discussed further in Sections 6 and 7. All of these reactions have nonlinear kinetics but they differ from the nonlinear

kinetics shown in Fig. 4.2(a) in that it is possible that a given normalised reaction rate corresponds to two values of the reaction extent; those in Fig. 4.2(a, c) show a unique reaction extent corresponding to a given normalised reaction rate.

The importance of these various kinds of reactions becomes apparent when the chemical reaction is coupled with transport of chemical components by fluid flow. If we consider a volume of rock

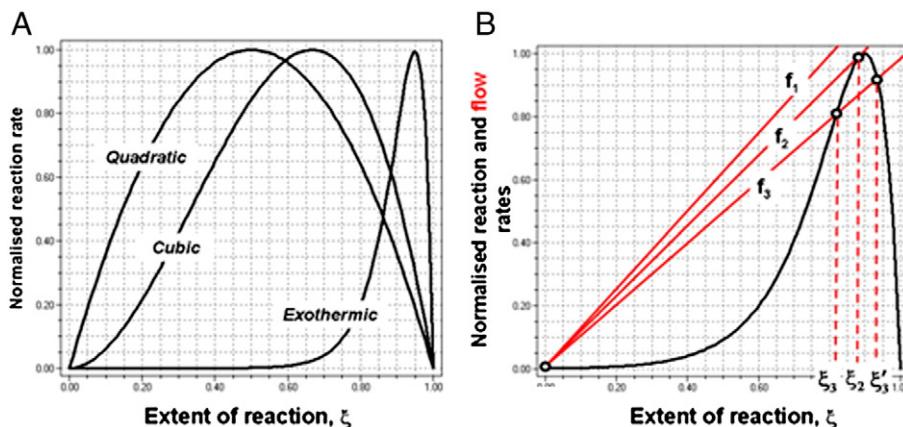


Fig. 4.3. Nonlinear chemical kinetics. (A) Normalised reaction rate versus extent of reaction for quadratic and cubic autocatalysis and for an exothermic first order reaction. (B) An open flow-controlled system. Normalised flow rates, f_1 , f_2 and f_3 , and normalised reaction rate for an exothermic first order reaction showing nonlinear system behaviour. The behaviour here is that of a *nonlinear chemical system*.

where fluid is flowing into and out of the volume at a volumetric flow rate of $q \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ with an inflow concentration of A equal to a_0 (with units mol m^{-3}) and an outflow concentration, a, then the contribution to the production rate of A within the volume of rock is

$$f = q\phi(a_0 - a) = q\phi a_0 \xi \quad (4.12)$$

with units [$\text{mol m}^{-2} \text{ s}^{-1}$]. We call this quantity, f, the net flow rate of A. A plot of the net flow rate against reaction extent is a straight line through the origin with slope $q\phi a_0$. If the flow rate equals the reaction rate then the system is at a stationary state (Fig. 4.2c). In Fig. 4.3(b) we show the relation of the net flow rate of A to the reaction rate for various values of f and of ξ and for an exothermic reaction of the type $A \rightarrow B$. The intersection of the line representing the net flow rate with the reaction rate curve defines a stationary state. A small change in f (which could result from a small fluctuation in ϕ) can result in a large change in behaviour. For a large net flow rate, f_1 , the only stationary reaction rate corresponds to $\xi = 0$. For a slightly smaller flow rate, f_2 , there results two stationary states corresponding to $\xi = 0$ and $\xi = \xi_2$. For a slightly smaller value of f, f_3 , there are three stationary states corresponding to $\xi = 0$, $\xi = \xi_3$ and $\xi = \xi'_3$. In systems of this type small changes in net flow rate can result in large changes in ξ and in the qualitative behaviour of the system. In contrast, for systems such as those illustrated in Fig. 4.2(a) small changes in flow rate result in small changes in ξ and the system behaviour remains qualitatively the same independently of the flow rate. We refer to systems such as that illustrated in Fig. 4.3(b) as *nonlinear chemical systems*.

Important features of nonlinear chemical systems are summarised in Fig. 4.4. Chemical reaction rates are influenced by a number of processes including heterogeneous kinetics (kinetics involving a solid surface), autocatalysis and exothermic behaviour. All of these processes can lead to multiple stationary states which in turn can induce fluctuations in temperature, fluid density, viscosity and surface tension and the porosity/permeability of the rock mass. All of these changes influence the Darcy velocity which alters the supply of reactants to the chemical reaction via the net flow rate, f. Thus strong feedback relations emerge in these nonlinear chemical systems. The development of multiple non-equilibrium stationary states can also

be influenced by chemical diffusion (Epstein and Pojman, 1998) and deformation (Ortoleva, 1994).

4.4. Stability of stationary states

Although stationary states are defined in flow controlled systems by the condition $\text{net flow rate} = \text{reaction rate}$ it is possible that the stationary state thus defined is not stable and the system, once perturbed, moves to another stationary state or oscillates about that stationary state. The term *stable* is used in the sense that if the system is perturbed by a small amount from the stationary state then it moves back to the stationary state; if the system is *unstable* the perturbation grows with time and the system moves to a new stationary state or oscillates. There is a formal mathematical procedure for establishing if a given stationary state is stable or unstable (Epstein and Pojman, 1998; Gray and Scott, 1990); we present a qualitative argument below.

Consider the flow diagram shown in Fig. 4.5 where the reaction rate is for an exothermic first order reaction and is given approximately by Gray and Scott (1990)

$$\frac{d\xi}{dt} = (1-\xi) \exp(B\xi) \quad (4.13)$$

where B is a constant taken here as $B = 20 \text{ s}^{-1}$.

The line representing the net flow rate intersects the reaction rate curve at the three stationary states P_1 , P_2 and P_3 . If, as in the argument presented above, the net flow rate is a linear function of the reaction extent, as expressed in Eq. (4.12), then for the steady state P_3 , a slight increase in the extent of the reaction (which corresponds to a slight decrease in the concentration of A) means that the net flow rate given by Eq. (4.12) increases whilst the reaction rate given by Eq. (4.13) decreases. Thus the system readjusts to return to the stationary state. A similar argument holds for P_3 if there is a slight decrease in the concentration of A. If on the other hand we consider P_2 , then again a slight increase in the reaction extent results in an increase in the net flow rate but also an increase in the reaction rate so that the increase in ξ is amplified. Thus P_2 is an unstable stationary state and of the two stationary states P_2 and P_3 , P_3 will be selected. In Section 6.2.2 we will see that the net flow rate is not always a linear function of the residence time τ and can be a quadratic

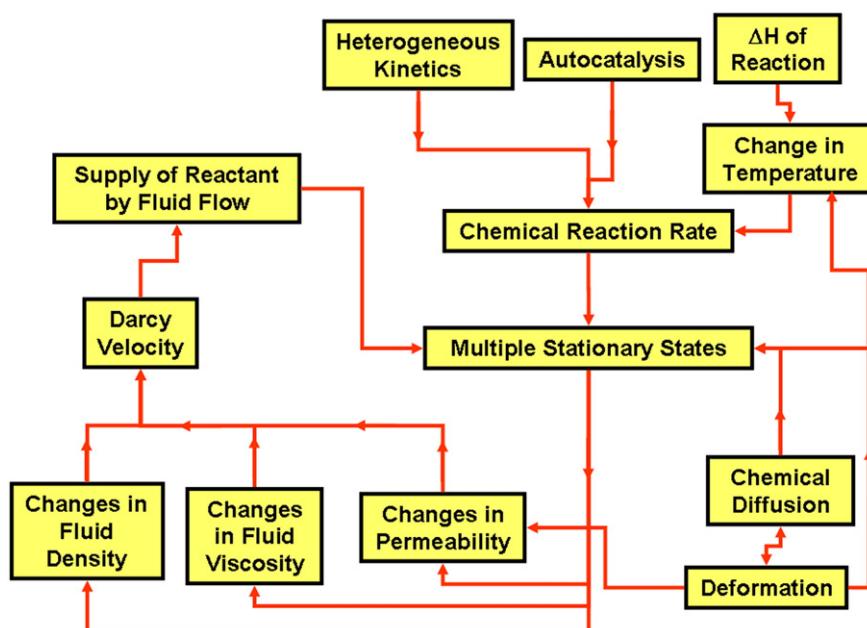


Fig. 4.4. Feedback loops in nonlinear chemical systems.

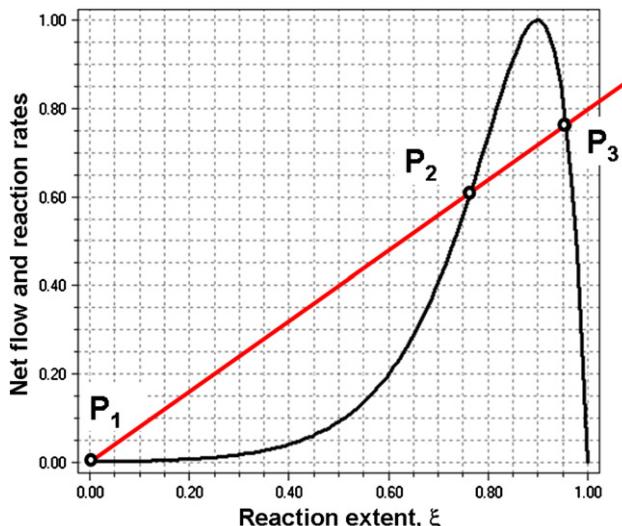


Fig. 4.5. A nonlinear chemical system with three non-equilibrium stationary states P_1 , P_2 and P_3 . An argument identical to that presented in Fig. 4.1(D) shows that P_3 is stable whereas P_2 is unstable.

function of τ . Then an increase in τ can lead to a decrease in net flow rate for a given reaction extent and the stability arguments need to take this into account. We consider such issues in Section 6.

5. Controls on Darcy fluid velocity, permeability and residence time within mineralising systems

5.1. The Darcy fluid velocity and permeability

An important parameter in the behaviour of any nonlinear open flow-controlled chemically reacting system is the residence time, given by Eq. (2.8), of an individual package of fluid in the system. This is controlled by the plumbing network supplying fluid and the plumbing network within the control volume. We are concerned in this paper with systems that are controlled by the flow of mass and heat. Typically a volume of rock many cubic kilometres in size within the crust of the Earth is subjected to infiltration of fluids which are initially hotter than the ambient temperature of the local crust. The chemical composition of these fluids is such that chemical reactions occur both in the fluid and between the fluid and the host rock; this region of reacting, infiltrating fluid becomes the *mineralising system*. The reacted, cooler fluids exit the system leaving behind a chemically altered, mineralised rock mass. Fluid flow can be described by Darcy flow in porous media or by Stokes flow within open pore or fracture networks. We will discuss flow in open pores and networks and its relation to Darcy flow in Part II. Darcy flow when steady can never be chaotic but Stokes flow can be laminar, chaotic or turbulent. In Part I we consider only steady Darcy flow. The residence time is controlled by the Darcy flux and the local porosity as indicated by Eq. (2.8). In hydrostatically pressured systems where the flow is controlled by a hydraulic potential (Fig. 4.1D) these quantities are easy to understand and are the basis of much modelling in environmental and ground water applications and in many near surface hydrothermal systems (Garven and Freeze, 1984a, 1984b; Steefel and Maher, 2009). However in lithostatically pressured systems subjected to regional stress regimes (such as orogenic gold and some IOCG systems) the controls on permeability are a little more complicated. If the fluid pressure gradient is close to hydrostatic as in most hydrothermal systems near to the surface of the Earth, and the fluid flow is driven by gradients in hydraulic potentials arising from topography or buoyancy then the presence of a relatively impermeable layer in the pathway of the fluid flow results in ponding of the fluid until some new pathway is developed. This is the process involved in the trapping of

oil and gas in hydrocarbon systems. However if the fluid flux is fixed, as in fluids released by a devolatilising reaction front (Hobbs and Ord, 2010; Phillips, 1991, pp 135–139) and the fluid pressure is near to lithostatic then the permeability must adjust to accommodate the imposed inexorable flux. In stressed material this can lead to fracturing, brecciation or the opening of vein and stockwork systems. These situations are common in orogenic gold (Dube and Goselin, 2007), IOCG (Bastrakov et al., 2007; Hunt et al., 2007; Oreskes and Einaudi, 1990) and epithermal (Henley and Berger, 2011) systems. Ponding in such systems can only be transient and short lived and persist until the permeability adjusts.

The infiltrating fluid is considered to have a Darcy velocity of $\hat{V} \text{ m}^{-2} \text{ s}^{-1}$. As indicated above, we immediately can distinguish two types of hydrothermal systems. First there are those where \hat{V} is controlled *inside* the system by the *internal* intrinsic distribution of permeability, K (in units m^2) and by an *externally imposed* gradient in hydraulic potential, ∇H (in units Pa m^{-1}). \hat{V} is then obtained from the conventional expression of Darcy's Law:

$$\hat{V} = -\frac{K}{\mu} \nabla H \quad (5.1)$$

where μ is the fluid viscosity (in units Pa s). Here K , μ and ∇H are independent variables, fixed by the geometry, chemistry and temperature of the system and the rocks that make up the system; \hat{V} is the dependent variable. Examples of these kinds of mineralising systems are those modelled by Garven and coworkers (Appold and Garven, 2000; Garven, 1985; Garven and Freeze, 1984a, 1984b; Raffensperger and Garven, 1995a, 1995b) and Murphy et al. (2008) for MVT and Irish style Pb-Zn deposits and for some unconformity-hosted U deposits where gradients in hydraulic potential are imposed by gradients in topography (Fig. 5.1a), or by fluid buoyancy.

The second type of mineralising system (Figs. 5.1b, c) is where \hat{V} is fixed at a constant rate by a fluid production mechanism (Hobbs and Ord, 2010; Phillips, 1991 pp 135–139). In this situation K must evolve in order to accommodate the imposed influx of fluid. Darcy's law is then better written (for constant fluid viscosity) as

$$K = -\mu \hat{V} / \nabla H = -\mu \hat{V} / (\nabla P^{\text{fluid}} - \rho^{\text{fluid}} g) \quad (5.2)$$

so that μ , ∇P^{fluid} , ρ^{fluid} and \hat{V} are now independent variables, fixed by the temperature and physical environment of the system, and K is the dependent variable. In these systems the environment controls \hat{V} . The environment may correspond to a rising devolatilising metamorphic reaction front (Phillips, 1991) or the expanding carapace of a crystallising magmatic body (Fig. 5.1c). The rate at which isotherms move, relative to the rock mass, in a devolatilising system releasing fluids at a reaction front or in a crystallising melt chamber that is releasing fluid as the magma crystallises, controls \hat{V} . The mechanics of such systems are discussed in Hobbs and Ord (2010) and Phillips (1991 pp 135–139). If the intrinsic permeability is large relative to $\mu \hat{V}$ then, provided ∇H is maintained in the mineralising system, the pore space must collapse to generate the required permeability that satisfies Eq. (5.2). If the intrinsic permeability is small relative to $\mu \hat{V}$ then fracturing or brecciation must ensue to generate the permeability required to accommodate \hat{V} . Mineralising systems of this second type are orogenic gold deposits such as Kalgoorlie and the Witwatersrand Au-U deposit and many IOCG deposits such as Olympic Dam and Ernest Henry all of which are characterised by widespread fracturing, veining and/or brecciation (Barnicoat et al., 1997; Cleverley and Oliver, 2005; Dube and Goselin, 2007; Haynes et al., 1995).

Once an upward fluid flow regime (comprising an upward flow and associated fluid pressure gradient and permeability) is established at the base of the mineralising system the permeability is self adjusting throughout the system provided the upward flow, \hat{V} , (measured in cubic metres per square metre per second) is maintained. As discussed

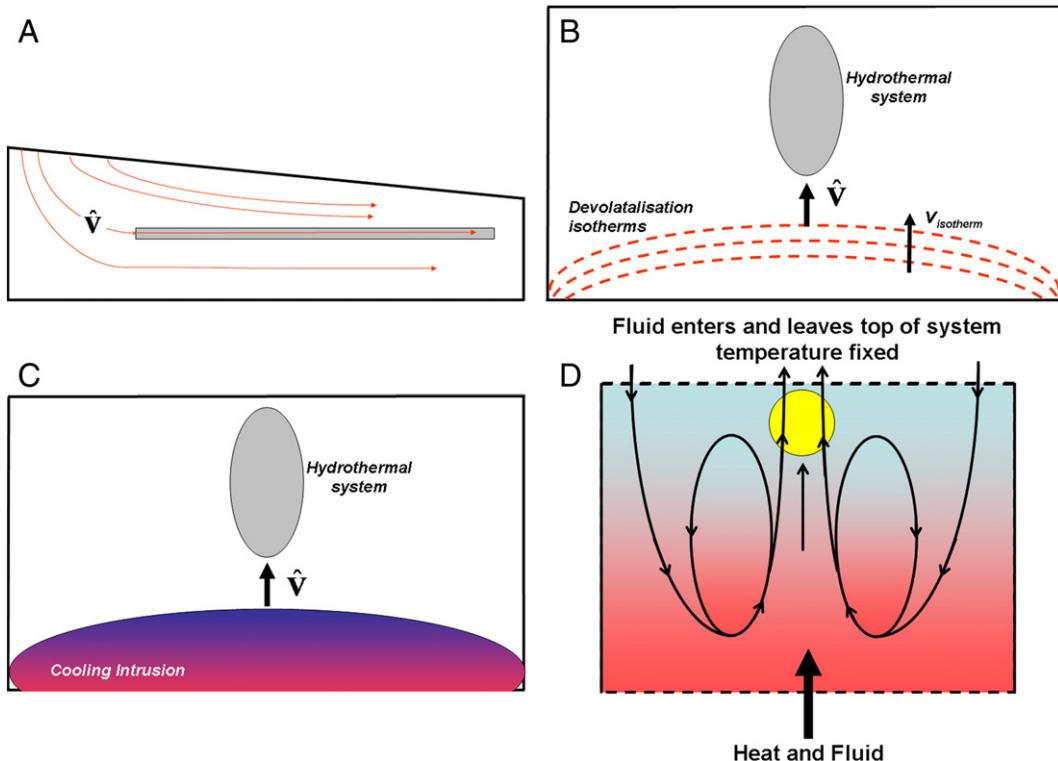


Fig. 5.1. The two types of control on Darcy fluid flux, \hat{V} , for hydrothermal systems. (A) Gradient in hydraulic potential defined by topographic gradient and the Darcy flux is controlled by the local permeability distribution. (B) and (C) Darcy flux controlled by velocity of moving isotherms or moving crystallisation front and imposed lithostatic hydraulic potential gradient. Permeability must adjust to accommodate this Darcy flux. (D) Darcy flux controlled from below but modified by a convective system. The convective system can only exist for a limited range of upward flow values (Zhao et al., 2008). The permeability must adjust to accommodate the resulting fluid flux.

by Zhao et al. (2008, pp 10–13), the permeability established at the base of the mineralising system acts as a pressure valve for the system above it. If this permeability is K_1 and the fluid encounters a region, of thickness L , above where the permeability is K_2 then, since for mass continuity the upward velocity \hat{V} must be the same in both regions,

$$\hat{V} = \left(\frac{\partial \hat{p}_1}{\partial z} - \rho_1^{\text{fluid}} g \right) \frac{K_1}{\mu_1} = \left(\frac{\partial \hat{p}_2}{\partial z} - \rho_2^{\text{fluid}} g \right) \frac{K_2}{\mu_2} \quad (5.3)$$

where g is the magnitude of the acceleration due to gravity and the fluid has densities ρ_1^{fluid} and ρ_2^{fluid} respectively in the two layers. μ_1 and μ_2 are the respective fluid viscosities, \hat{p}_i is the fluid pressure and z is the vertical distance. It follows that if $\rho_1^{\text{fluid}} = \rho_2^{\text{fluid}}$ and $\mu_1 = \mu_2$

$$\frac{\partial \hat{p}_2}{\partial z} = \frac{K_1}{K_2} \frac{\partial \hat{p}_1}{\partial z} + \rho^{\text{fluid}} g \left(1 - \frac{K_1}{K_2} \right) \quad (5.4)$$

so that $\frac{\partial \hat{p}_2}{\partial z}$ approaches the fluid hydrostatic pressure gradient, $\rho^{\text{fluid}} g$, as K_2 becomes larger than K_1 . For instance if $K_2 = 10 K_1$ and $\frac{\partial \hat{p}_2}{\partial z}$ is lithostatic then $\frac{\partial \hat{p}_2}{\partial z}$ is only 1.17 times the hydrostatic fluid pressure gradient. Conversely, if $K_2 > K_1$ then the fluid pressure gradient in layer 2 becomes greater than lithostatic in order to accommodate \hat{V} . If $K_2 = 0.1 K_1$ then $\frac{\partial \hat{p}_2}{\partial z}$ is 6.7 times the lithostatic gradient and the rock mass must fracture, brecciate or form open vein networks or stockworks in order to reduce the gradient back to a fluid pressure that the rock mass can mechanically sustain.

When the pressure gradient decreases below lithostatic, although the new average pressure in any particular compartment must be lithostatic, the pressure gradient relaxes to near hydrostatic on the

time scale of $(L^2/\kappa^{\text{fluid}})$ where κ^{fluid} is the fluid diffusivity and is given (Phillips, 1991) by:

$$\kappa^{\text{fluid}} = \frac{KV_P^2\rho^{\text{fluid}}}{\mu\phi} \quad (5.5)$$

where V_P is the P-wave velocity in the fluid, and ϕ is the porosity.

This relaxation in fluid pressure gradient produces compressive stresses at the base of the compartment and effective tensile stresses at the top as discussed by Zhao et al. (2008). The maximum height, L_{critical} , of a body of rock that can support a fluid pressure gradient is

$$L_{\text{critical}} = \frac{\bar{\sigma}_{\text{tensile}} + \bar{\sigma}_{\text{compressive}}}{(\rho_{\text{rock}} - \alpha\phi)\bar{g}} \quad (5.6)$$

where $\bar{\sigma}_{\text{tensile}}$ and $\bar{\sigma}_{\text{compressive}}$ are the tensile and compressive strengths of the rocks comprising the mineralising system. α is a parameter that measures how far the fluid pressure gradient is above hydrostatic. $\alpha = 1$ for a hydrostatic hydraulic gradient and $\alpha = 2.7$ for a lithostatic hydraulic gradient with average rock density 2700 kg m^{-3} . Thus, if $(\bar{\sigma}_{\text{tensile}} + \bar{\sigma}_{\text{compressive}}) = 50 \text{ MPa}$, say, then $L_{\text{critical}} \approx 3 \text{ km}$ for a hydrostatic fluid pressure gradient. If the height of the relaxed alteration zone is greater than L_{critical} then the base of the column collapses and the top localises as fractures resulting in compaction of the rock mass at the base and expulsion of fluid at the top of the compartment in a manner similar to that considered by Connolly and Podladchikov (1998). Thus thick alteration zones compact from the base upwards and release fluid at the top. It is to be emphasised that this compaction process is the result of fluid migration and not the cause as is sometimes proposed in fluid systems (McKenzie, 1984).

Following the above discussion the more permeable unit must compact from its base upwards until the permeability reaches K_1

and the height is less than L_{critical} . Conversely if $K_2 < K_1$ the fluid pressure must in principle be greater than lithostatic and this pressure induces fracturing until the permeability reaches K_1 . Thus the permeability within the hydrothermal system is self-adjusting and tends towards a permeability distribution that can accommodate the flux \hat{V} established at the base of the hydrothermal system.

On the other hand, if the fluid is rising in a zone that has a constant permeability, K_1 , and the viscosity changes from μ_1^{fluid} to μ_2^{fluid} higher in the system because the temperature and/or the chemical composition/volatile content of the fluid changes then

$$\frac{\partial \hat{p}_2}{\partial z} = \frac{\mu_2}{\mu_1} \frac{\partial \hat{p}_1}{\partial z} + \rho^{\text{fluid}} g \left(1 - \frac{\mu_2}{\mu_1} \right) \quad (5.7)$$

so that, for instance, a 10 fold increase in viscosity for a lithostatic value of $\frac{\partial \hat{p}_1}{\partial z}$ results in a fluid pressure gradient that is >10 times the lithostatic gradient which means that the fluid pressure at the top of this part of the transport zone increases dramatically. This is presumably capable of initiating brittle fractures and brecciation in the region above. Note that the viscosity of water decreases rapidly with increasing temperature (Fig. 5.2) at crustal pressures in the range 0 °C to ~600 °C (Abramson, 2007); the variation in viscosity, μ , with temperature is given approximately by $\mu = A [10^{B/(T-C)}]$ where $A = 2.414 \times 10^{-5}$ Pa s, $B = 247.8$ K and $C = 140$ K. In this range even a temperature decrease of the fluid of 10 °C is sufficient to induce fracture in a flow controlled system already close to failure (Fig. 5.2B). The same lines of argument apply for changes in fluid density induced by changes in temperature or chemical composition although the effect is much smaller. Similar arguments follow for large fluid temperature changes for a system with an initial fluid pressure gradient close to

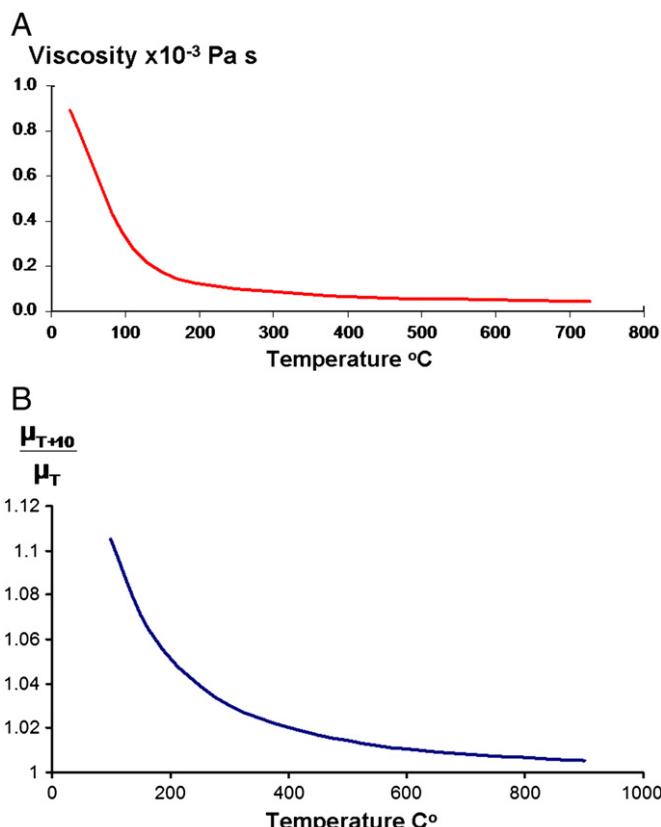


Fig. 5.2. Variation of the viscosity of pure water with temperature. (A) Viscosity versus temperature. (B) Change in the viscosity of water for a 10 degrees Centigrade increase in temperature.

hydrostatic since a three fold increase in the hydrostatic gradient is ≈1.1 times the lithostatic gradient.

Thus it is of fundamental importance to distinguish between open flow systems that are flow controlled (constant flux) and those that are hydraulic-potential controlled (constant hydraulic potential). The evolution of these two types of flow systems is quite different. The flow-controlled systems must adjust their permeability structure (and hence porosity structure) to account for changes in the physical characteristics (density, viscosity, pressure) of the fluid. This can promote widespread fracturing, veining and brecciation. The hydraulic head-controlled systems must adjust their permeability structure to account for clogging of their porosity by new minerals if the system is to continue to operate and such adjustments may be solely chemical in nature (Merino and Canals, 2011).

An additional reason for making a distinction between these two types of systems lies in the observation by Niven (2010b) that at least in simple pipe systems these two types of flow systems may have contrasted types of entropy production extrema principles that select between steady states and bistable, oscillatory and chaotic modes of operation of the system. This issue will be considered in Section 6.

5.2. The residence time of fluids in mineralising systems

Once \hat{V} is established within the mineralising system then the fluid velocity, v , is given by $v = \hat{V}/\phi$ where ϕ is the porosity. If we consider a reacting cube of material of side length L , then the residence time for fluid in the system is

$$\tau = L\phi/\hat{V}. \quad (5.8)$$

If τ is large compared to timescales associated with other processes such as deformation, heat flow and chemical reactions, then the system is commonly considered to be at "local equilibrium" or "close to" equilibrium. If the residence time is small then equilibrium is never attained so long as the flow is maintained. In models of MVT deposits (Garven and Freeze, 1984a, 1984b) typical values of \hat{V} and ϕ are 1×10^{-7} m s⁻¹ and 0.1 respectively and $L \approx 1$ km, giving $\tau = 10^9$ s or approximately 32 years (1 year = 3.16×10^7 s). In a lithostatically pressured system such as an orogenic gold deposit with $K = 10^{-16}$ m², $\phi = 10^{-2}$ and $L \approx 100$ m as an example, $\tau = 5.9 \times 10^8$ s although the work of Cox (1995, 1999), Miller and Nur (2000), and Sibson (1987, 1992) would suggest transient periods of flow where the permeability is increased thus decreasing τ at least by an order of magnitude.

Many mineral hydrothermal reactions involve processes such as reaction between chemical species operating in a fluid (commonly referred to as involving *homogeneous kinetics*) and coupled processes such as reaction, dissolution and precipitation operating at the interface between the fluid and a mineral (commonly referred to as involving *heterogeneous kinetics*). The units for these two types of reactions are different; the units for homogeneous reactions are s⁻¹ (or mol s⁻¹) whereas those for heterogeneous reactions (since they involve the surface area available for reaction) are m⁻² s⁻¹ (or moles m⁻² s⁻¹). The rates of homogeneous reactions are generally quite fast relative to heterogeneous reaction rates. Typical homogeneous rate constants lie in the range 10^{-2} to 10^{-1} s⁻¹ (Lasaga, 1981) giving time scales, $\tau^{\text{homogeneous}}$ in the range 10 to 100 s. Heterogeneous rate constants lie in the range 10^{-10} to 10^{-8} mol m⁻² s⁻¹ (Lasaga, 1981). The areas of reacting surfaces are difficult to measure and any calculation of surface areas is strongly model-dependent. Upper estimates lie in the range 10^2 to 10^3 m² mol⁻¹ giving values for the time scales associated with heterogeneous reactions, $\tau^{\text{heterogeneous}}$, in the range 10^8 to 10^5 s. Thus the time scales associated with heterogeneous reactions may approach the residence times quoted above and if punctuated increases in permeability occur (Miller and Nur, 2000) the residence times may be smaller than the heterogeneous reaction time

scales; for steady flows chemical reaction time scales are smaller than the quoted residence times. Long residence times are commonly used as a reason for adopting an equilibrium approach to modelling mineralising systems (Steefel and Lasaga, 1994; Steefel and Maher, 2009).

However we will see that such reasoning is based on models where the chemical system is linear. Once this assumption is relaxed open flow systems may be far from equilibrium for very large residence times and may never reach equilibrium. As we will see below, there is a fine trade off between net flow rate (or residence time) and supply of nutrient for the reaction to proceed. If the net flow rate is too high the residence time is not sufficient for significant reaction to occur. If the net flow rate is too small, the residence time is large but again the supply of nutrient may be too small for the reaction to proceed. Between these two extremes the system may be obtaining the required nutrient for significant reaction rates but many different non-equilibrium stationary states can exist for nonlinear reaction systems and the system may even oscillate around one or more of these states indefinitely.

The important parameter controlling these various types of behaviour is the quantity $q\phi a_0$ defined in association with the net flow rate, f , in Eq. (4.12) rather than the time scale τ defined in Eq. (5.8). The net flow rate, f , represents the slope of the flow rate line in Figs. 4.2(c), 4.3(b) and 4.5.

6. Behaviour of nonlinear chemical systems

Nonlinear chemical systems display a large range of behaviour ranging from stable and unstable stationary states, to chaotic spatial and temporal oscillations in both composition and temperature (Epstein and Pojman, 1998; Gray and Scott, 1990; Imbihl, 2009; Ross, 2008; Scott, 1994). Although hydrothermal systems are open flow thermodynamic systems much of the behaviour of interest is exhibited by simple first order chemical reactions such as $A \rightarrow B$ in isolated systems as long as some other process operates to produce feedback on the reaction rate. Such processes include the influence of the heat of reaction on the reaction rate constant (Gray and Scott, 1990), various competitive processes that may operate during chemical reactions at crystal interfaces (Ertl, 2009; Imbihl and Ertl, 1995)

and processes associated with deformation (Ortoleva, 1994). One might expect that the behaviour of open flow systems would be intrinsically more complicated than that of isolated systems. Although this is true in detail much of the behaviour of open flow systems is apparent in isolated systems and the mathematical treatment is sometimes much simpler for isolated systems. For this reason we first look at one of the simplest of systems from a mathematical point of view that exhibits much of the behaviour seen in isolated systems. This is the operation of cubic autocatalytic reactions (Sections 4 and 6.1). The essential difference between isolated and open flow systems is that isolated systems, although exhibiting unstable behaviour for some of their life, must ultimately proceed smoothly to equilibrium whereas open flow systems can in principle be kept in stationary states far from equilibrium indefinitely so long as mass and energy are supplied to the system and reactants within the control volume are not exhausted. In order to bring out the essential behaviours of nonlinear chemical systems we first look at isothermal autocatalytic reactions in isolated systems (Section 6.1), then isothermal autocatalytic systems in open flow systems (Section 6.2), exothermic first order reactions in open flow systems (Section 6.3) and parallel, chemically uncoupled, exothermic first order reactions in open flow systems (Section 6.4). These series of examples display all of the known behaviours exhibited by nonlinear chemical systems and are summarised in Fig. 6.1.

6.1. Autocatalytic reactions in isolated systems

Networked chemical reactions (Carmichael, 1969) that involve changes in redox state are particularly susceptible to instabilities (Epstein and Pojman, 1998). One reason for this seems to lie in that many redox reactions can be expressed in an autocatalytic manner. Thus the oxidation of Fe^{2+} can be written:



We take an example where a mineral, P, reacts in an isolated system (Fig. 6.1a) to produce another mineral, C, $P \rightarrow C$ and in the process P dissolves in an inter-granular fluid to contribute Fe^{2+} to that fluid. An example could be siderite reacting to produce haematite.

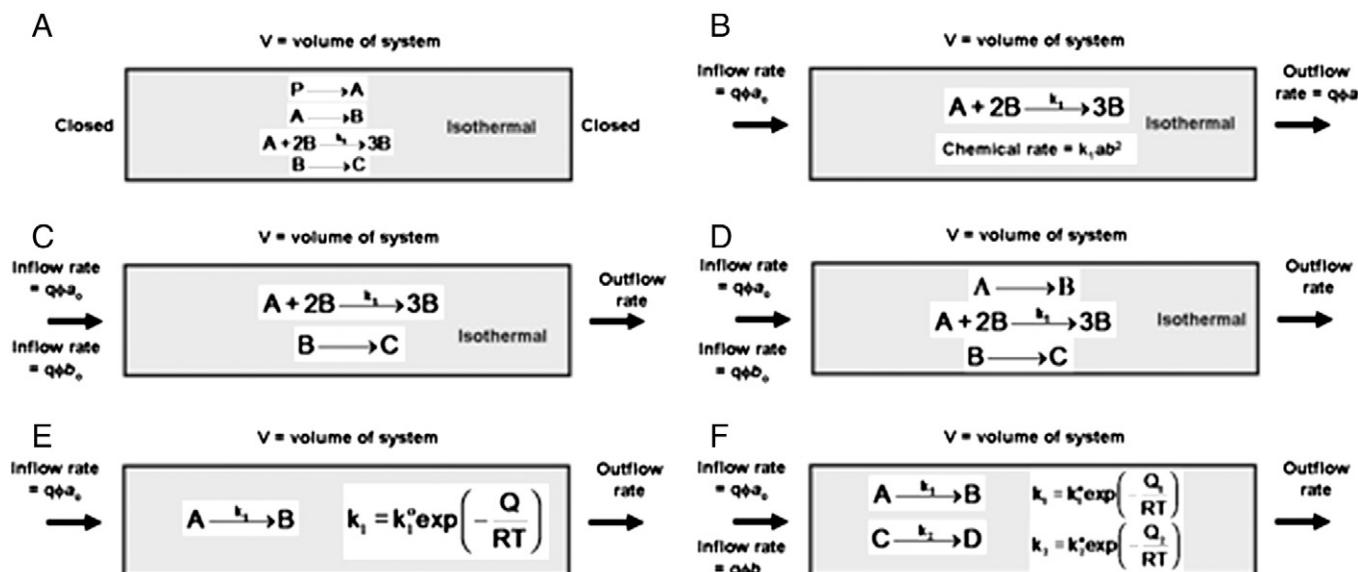
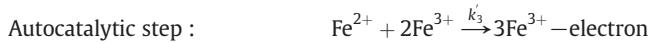
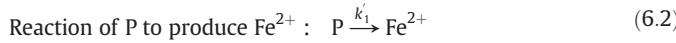


Fig. 6.1. The various simple models considered here. (A) Isolated cubic autocatalytic isothermal system. (B) Open flow-controlled isothermal cubic autocatalytic system with only influx of A. (C) Same as (B) but the reaction B decays to C. Two cases are considered: influx of A only and influx of both A and B. (D) Same as (C) but the reaction $A \rightarrow B$ is added. (E) Single first order exothermic reaction $A \rightarrow B$. (F) Two parallel chemically uncoupled exothermic reactions.

The Fe^{2+} is oxidised to Fe^{3+} at an interface via a catalytic, and in solution via a non-catalytic, step. A set of networked reactions that describes the redox part of the reaction is:



where the k_i' are the reaction rates for the four reactions.

The set of equations that describes the coupling between these reactions is:

$$\begin{aligned} \frac{\partial P}{\partial t} &= -k_1 P \\ \frac{\partial [\text{Fe}^{2+}]}{\partial t} &= k_1 P - k_2 [\text{Fe}^{2+}] - k_3 [\text{Fe}^{2+}][\text{Fe}^{3+}]^2 \\ \frac{\partial [\text{Fe}^{3+}]}{\partial t} &= k_2 [\text{Fe}^{2+}] + k_3 [\text{Fe}^{2+}][\text{Fe}^{3+}]^2 - k_4 [\text{Fe}^{3+}] \\ \frac{\partial C}{\partial t} &= k_4 [\text{Fe}^{3+}] \end{aligned} \quad (6.3)$$

where for clarity square brackets have been used to indicate the concentration of Fe^{2+} and Fe^{3+} and the k_i are functions of the k_i' s and of the concentrations of any other components that may be involved in the reactants. Solutions to these equations are shown in Fig. 6.2 where the system oscillates in time with respect to the concentrations of Fe^{2+} and Fe^{3+} in solution; the reactant, P, and the product, C, proceed monotonically to equilibrium.

Reactions of this type are important for instance in the precipitation of gold if such a process is coupled with redox reactions. Thus the reaction involving the production of pyrite:



coupled to the precipitation of gold:

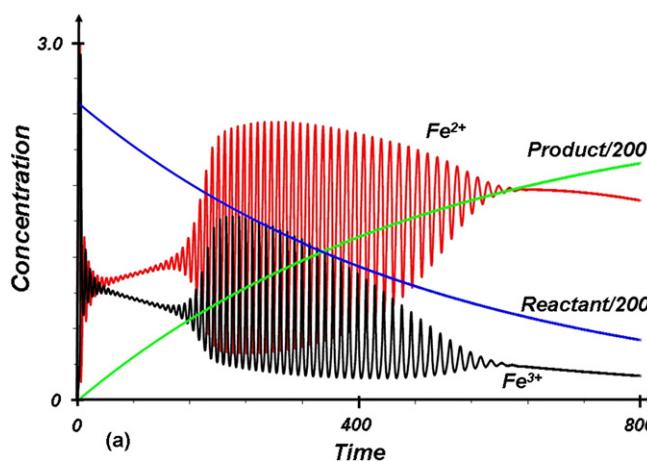


Fig. 6.2. The behaviour of the isolated system (6.2). The concentrations of the reactant (P) and the product C proceed monotonically to equilibrium. The intermediaries, Fe^{2+} and Fe^{3+} , oscillate before proceeding monotonically to equilibrium. Produced using software in Boyce and DiPrima (2005).

means that the precipitation of gold is linked to the concentration of Fe^{2+} and hence oscillates as Fe^{2+} oscillates (see also Henley and Berger, 2000). The behaviour is clearly also pH dependent. The general behaviour of the isothermal cubic autocatalytic process is formalised by Gray and Scott (1990). An important aspect of this classical system is that if diffusion of Fe^{2+} and Fe^{3+} is coupled with Eq. (6.3) then spatial patterning (Turing patterns) develops. This latter situation is discussed by Fisher and Lasaga (1981). Such spatial patterning would be expressed as redox fronts in hydrothermal systems with no need for fluid mixing in the system.

6.2. Autocatalytic, isothermal reactions in open flow systems

This system is shown in Fig. 6.1(b, c, d) and is discussed by Gray and Scott (1990, Chapter 6). In the following we distinguish four cases of reactions of A and B involving cubic autocatalysis of increasing complexity: (i) only A entering the system, (ii) decay of B to a new product, C, (iii) both A and B entering the system and (iv) coupling of the reaction to the reaction $A \rightarrow B$.

6.2.1. Cubic autocatalysis with only A entering the system

In order to show that one uncoupled isothermal chemical reaction can become unstable due to coupling with fluid flow in an open flow system we consider the cubic autocatalytic reaction:



The system consists of a flow controlled reactor as shown in Fig. 6.1(b) where a fluid containing A is mixed with B within the reactor and the outflow is the product of the reaction. We concentrate the discussion on the evolution of A. The initial concentration of A in the inflow stream is a_o ; there is no inflow of B which has an initial concentration of b_o within the reactor.

The concentration of A within the reactor, a , is determined by three quantities: (i) the inflow rate of A: $r_{in} = q\phi a_o$, where q is the volume in-flow rate. (ii) The outflow rate of A: $r_{out} = q\phi a$. (iii) The total rate of conversion of A to B: $r_{chem} = V k_1 ab^2$. Thus,

$$V \frac{da}{dt} = q\phi a_o - q\phi a - V k_1 ab^2. \quad (6.8)$$

The concentrations of A and B are related by $a_o + b_o = a + b$ and so

$$\frac{da}{dt} = k_{flow}\phi(a_o - a) - k_1 a(a_o + b_o - a)^2 \quad (6.9)$$

where we have written k_{flow} for q/V . The concentration of A now evolves to a stationary state value a_{ss} where the chemical production rate balances the inflow and outflow rates so that $\frac{da}{dt} = 0$ and the system is at a stationary state. This non-equilibrium stationary state can be maintained indefinitely so long as the quantity $k_{flow}\phi a_o$ is maintained as the inflow stream and B is not exhausted. Stationary states in the system can be found as solutions to

$$k_{flow}\phi(a_o - a_{ss}) - k_1 a_{ss}(a_o + b_o - a_{ss})^2 = 0. \quad (6.10)$$

An instructive way to explore these solutions is the use of a flow diagram that plots the two rates, net inflow rate and the chemical reaction rate, as functions of the extent of the reaction, $\xi = (a_o - a)/a_o$. The net flow rate, v is

$$v = k_{flow}\phi(a_o - a) = k_{flow}\phi a_o \xi \quad (6.11)$$

and the chemical reaction rate is

$$R = k_1 a(a_0 + b_0 - a)^2 = k_1 a_0(1 - \xi)(b_0 + a_0 \xi)^2. \quad (6.12)$$

Points of intersection of Eqs. (6.11) and (6.12) on the flow diagram (Fig. 6.3) where $R=v$ correspond to solutions to Eq. (6.10) and hence are stationary state solutions. Note that in many instances the line defined by Eq. (6.11) intersects the curve defined by Eq. (6.12) in two points showing that two stationary states exist in addition to another which in this case corresponds to the origin; such systems are said to exhibit *bistability*. Fig. 6.3 shows some of these solutions for which bistability exists. Gray and Scott (1990, p 21) show that bistability exists for $a_0 > 8b_0$. An interpretation of Fig. 6.3 in terms of processes operating within the system is given in Fig. 6.4. The important point is that the behaviour of the system depends on the value of $k_{\text{flow}}\phi a_0$ (or the slope of the red lines in Figs. 6.3 and 6.4) and so for constant fluid flow rate and a given concentration of the reactant A, the behaviour of the system will vary with the local porosity which ultimately is expressed as variations in the local permeability.

Gray and Scott (1990, Chapter 6) also consider the influence of adding reversibility and influx of B to reaction (6.6). The basic behaviour remains as described above. Bistability remains as the essential

characteristic of the nonlinear behaviour and no oscillatory behaviour emerges.

6.2.2. Cubic autocatalysis with decay of B

We now consider a slight change in the flow controlled system where the component B decays to a new product C (Fig. 6.1c) so that the complete set of reactions is



Only A is fed to the system but A, B and C are extracted. The initial concentration of C is taken to be zero so that $c = (a_0 + b_0) - (a + b)$. The rate equations now become

$$\begin{aligned} \frac{da}{dt} &= q\phi(a_0 - a) - k_1 ab^2 \\ \frac{db}{dt} &= q\phi(b_0 - b) + k_1 ab^2 - k_2 b. \end{aligned} \quad (6.14)$$

We define the dimensionless groups α , β and κ_2 as

$$\alpha = \frac{a}{a_0}, \beta = \frac{b}{a_0}, \kappa_2 = \frac{k_1}{k_2 a_0^2}. \quad (6.15)$$

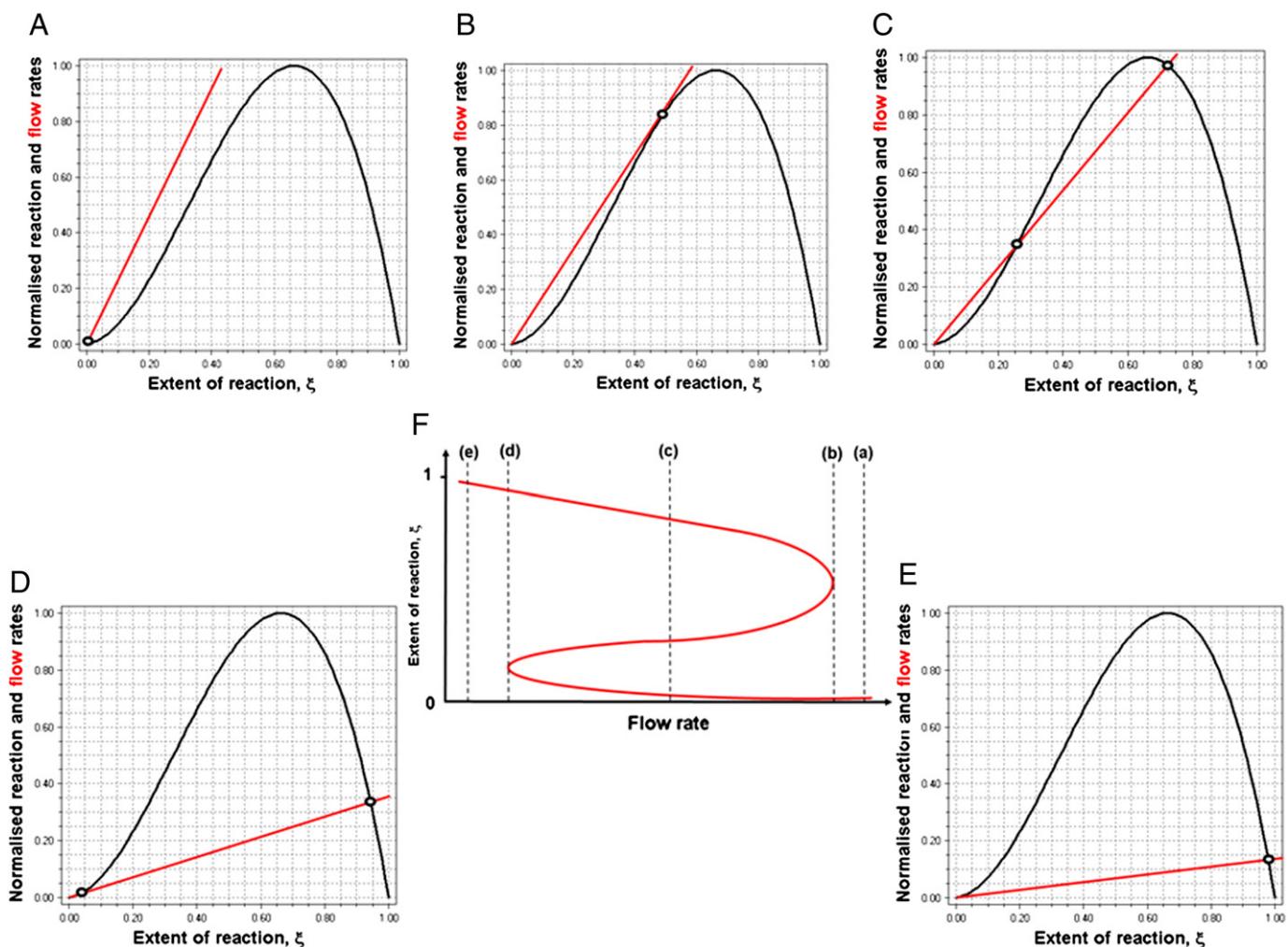


Fig. 6.3. Flow diagrams showing the origin of bistability for cubic autocatalysis in an open flow-controlled system. The red line in (A) through to (E) is the net flow rate whilst the black curve is the chemical reaction rate. (F) Stationary states for the cubic autocatalytic reaction with flow. The red line is the plot of extent of reaction against flow rate showing the presence of three stationary states between (B) and (D).

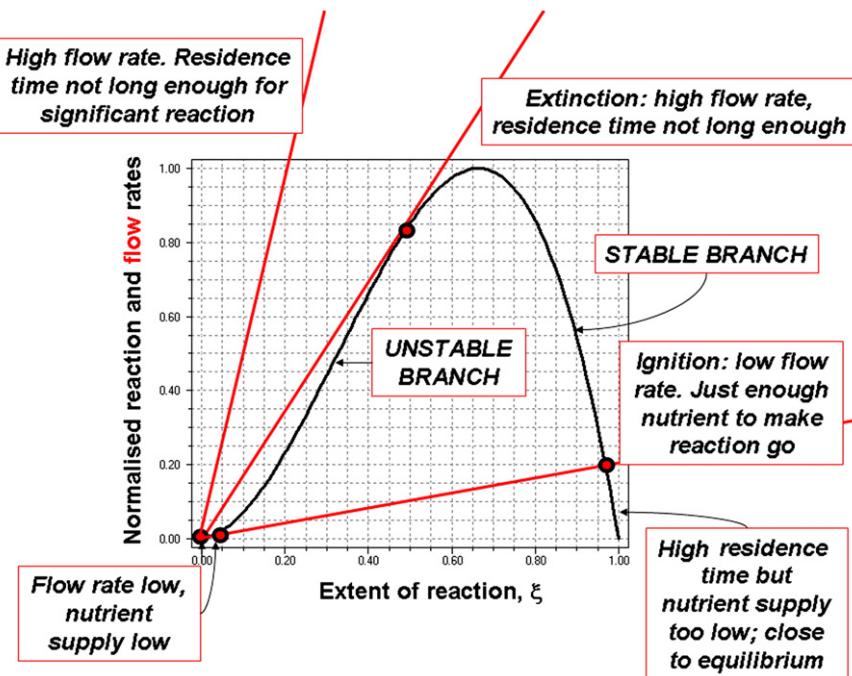


Fig. 6.4. Summary diagram showing the behaviour of the cubic autocatalytic reaction (6.6) in a flow controlled system.

The mass balance equations (6.14) become

$$\begin{aligned} \frac{d\alpha}{dt} &= q\phi(1-\alpha) - \alpha\beta^2 \\ \frac{d\beta}{dt} &= q\phi(\beta_0 - \beta) + \alpha\beta^2 - \kappa_2\beta. \end{aligned} \quad (6.16)$$

The stationary state concentration β_{ss} is given by

$$\beta_{ss} = \frac{1 + \beta_0 - \alpha_{ss}}{1 + (\kappa_2/q\phi)}. \quad (6.17)$$

We substitute Eq. (6.17) into the equation expressing the stationary state of α : $\frac{d\alpha}{dt} = 0$ to obtain an equation for the stationary state of the system:

$$\begin{array}{ccc} \text{Flow rate} & - & \text{Reaction rate} \\ \boxed{} & & \boxed{} \end{array} = 0 \quad (6.18)$$

$$\frac{(1 + \kappa_2 \tau_{res})^2}{\tau_{res}} (1 - \alpha_{ss}) - \alpha_{ss} (1 + \beta_0 - \alpha_{ss})^2 = 0.$$

As opposed to the situation where there is no decay of B the flow rate is now a quadratic function of the residence time although still a linear function of the extent of the reaction. This means that the slope of the flow line on a flow diagram is steep at low residence times and decreases initially as the residence time increases. However the slope reaches a minimum at

$$\frac{dv}{d(1-\alpha_{ss})} = 4\kappa_2 \quad \text{when } \tau_{res} = \frac{1}{\kappa_2} \quad (6.19)$$

and then increases again as the residence time increases. If $b_0 = 0$ then Eq. (6.18) becomes

$$\frac{(1 + \kappa_2 \tau_{res})^2}{\tau_{res}} (1 - \alpha_{ss}) - \alpha_{ss} (1 - \alpha_{ss})^2 = 0 \quad (6.20)$$

and a plot of extent of reaction ($1 - \alpha_{ss}$) against the residence time becomes that shown in Fig. 6.5(a) together with $(1 - \alpha_{ss}) = 0$ (Fig. 6.5b). Instead of the S-shaped curve of Fig. 6.3(f) we now have a closed curve known as an *isola* together with the straight line $(1 - \alpha_{ss}) = 0$. In this system it is not possible to have very long residence times that approach complete reaction and hence equilibrium. There is a minimum flow rate corresponding to a finite extent of reaction. This minimum flow rate is given by Eq. (6.19) and is a function of the input concentration of A.

Although the stationary states are now defined by Eq. (6.20) not all of them are stable. Gray and Scott (1990, Chapter 6) discuss the stability of the system in some detail and show that the lowest branch $\xi = 0$ is always stable as is part of the uppermost branch. However the lowest part of the isolas is always unstable together with part of the uppermost branch as shown in Fig. 6.5(b). Moreover the point that marks the loss of stability on the uppermost branch corresponds to a complete change in behaviour of the system. This is known as a Hopf bifurcation which represents the appearance or disappearance of periodic behaviour associated with the change in stability (Guckenheimer and Holmes, 1986; Wiggins, 2003). In general a Hopf bifurcation can be supercritical or subcritical as shown in Fig. 6.6(a). If one plots the behaviour of a system in phase space (a phase portrait) as shown in Fig. 6.6 then a supercritical Hopf bifurcation is represented by oscillations of decreasing amplitude that ultimately settle into a limit cycle. The system can also start at a limit cycle and oscillate to a fixed point. A subcritical Hopf bifurcation can begin at a fixed point and oscillate to a limit cycle or start at a limit cycle and evolve with increasing amplitude of oscillations. Both types of behaviour are possible on the uppermost branch of the isolas and some phase portraits are shown in Fig. 6.6(b). One type of behaviour is for the system to undergo a Hopf bifurcation which ends on the stable lowermost branch corresponding to $\xi = 0$. Thus the behaviour of this relatively simple system is complex and quite different forms of behaviour emerge with small changes in residence time (and hence of porosity). Thus in this system with constant supply of A, adjacent pieces of rock with slight fluctuations in porosity can have quite contrasted behaviours: one can undergo oscillations of chemical composition at high values of the reaction extent whilst immediately adjacent areas show no reaction at all.

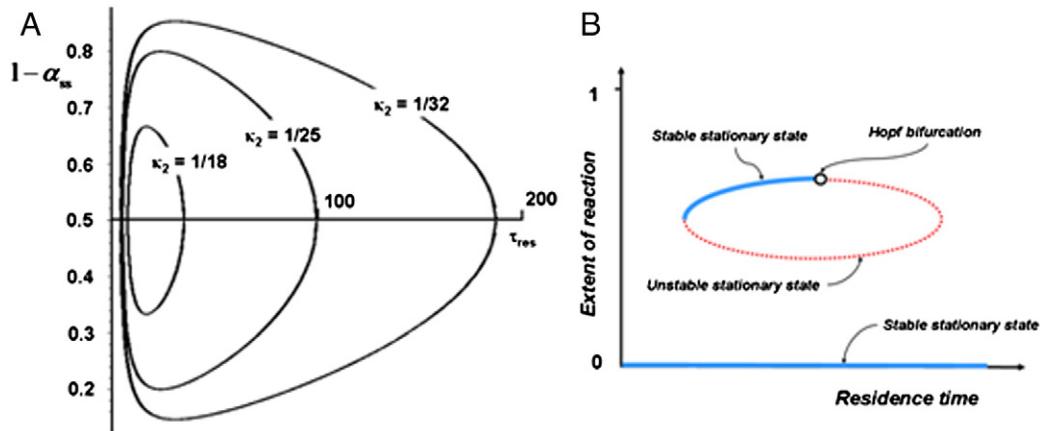


Fig. 6.5. An isola as a stationary state locus for reactions with no autocatalytic inflow and $\kappa_2 < 1/16$. (A) Isola for various values of κ_2 . In addition the line $1 - \alpha_{ss} = 0$ exists as a solution for all conditions. (B) Stability of steady states. Blue represents stable steady states, dotted red are unstable steady states. Open circle is a Hopf bifurcation. See Gray and Scott (1990, Chapter 6) for discussion and details.

This has nothing to do with whether fluid has or has not accessed the relevant parcel of rock; it is controlled solely by the local flow rate and hence the local permeability.

6.2.3. Cubic autocatalysis with A and B entering the system

The next step in complexity is to add an inflow of concentration of B, that is, $b_0 \neq 0$; then the response becomes much more complicated. The gradient of the flow line is still given by the first term in Eq. (6.18) but now the reaction rate is a function of β_0 . An example of the flow diagram and the resulting stationary state loci are given in Fig. 6.7 where both isola and mushrooms (Fig. 6.7F, H) can emerge. As in the case of cubic autocatalysis with $b_0 = 0$ (Figs. 6.6 and 6.7) not all of the stationary states shown in Fig. 6.7 are stable and the behaviour of the system is better demonstrated in Fig. 6.8 where dotted lines show unstable states and black dots show Hopf bifurcations. The lines emerging from Hopf bifurcations illustrate the extent and amplitudes of oscillations that emerge or die at the Hopf bifurcation. Again it is clear that slight fluctuations in the residence time can induce

dramatic changes in system behaviour such as the sudden emergence of oscillatory behaviour from a stable stationary state or a sudden drop or increase in reaction extent.

6.2.4. Cubic autocatalysis coupled with the reaction $A \rightarrow B$

We now add the reaction $A \rightarrow B$ to reaction (6.13) as shown in Fig. 6.1(d). The result (Gray and Scott, 1990, Chapter 6) is a new range of behaviour as shown in Fig. 6.9. The stationary states define isola and mushrooms but now a new pattern arises called a *breaking wave* (Fig. 6.9d) together with a *single hysteresis loop* (Fig. 6.9c). As in previous examples both stable and unstable stationary states are represented in Fig. 6.9 together with Hopf bifurcations. The system is discussed in detail by Gray and Scott (1990, Chapter 6).

6.3. First order exothermic reactions in open flow controlled systems

The case of a single first order exothermic reaction (Fig. 6.1e) would seem to be much simpler than the isolated systems involving

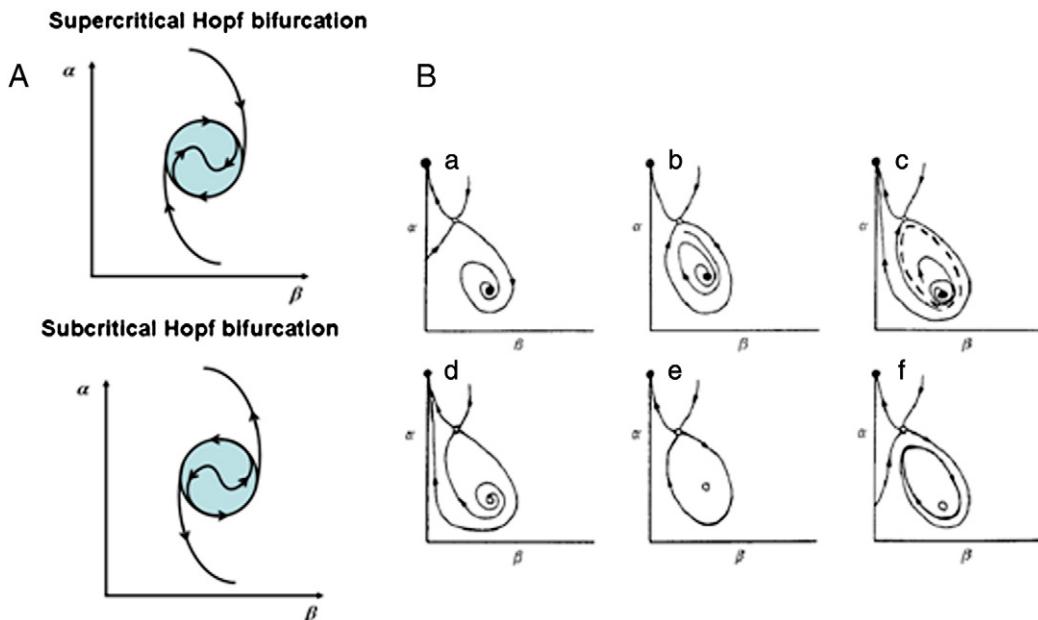


Fig. 6.6. Phase portraits. (A) Supercritical and subcritical Hopf bifurcations. (B) Phase portraits associated with Hopf bifurcations on the uppermost branch of the isola of Fig. 6.5(b). Full black circles are stable stationary states whereas open circles in the lower parts of (d), (e) and (f) are unstable stationary states. Notice that in all plots the system can readily converge on a stable stationary state where $\beta = 0$. See Gray and Scott (1990, section 8.3.7 for a discussion and details).

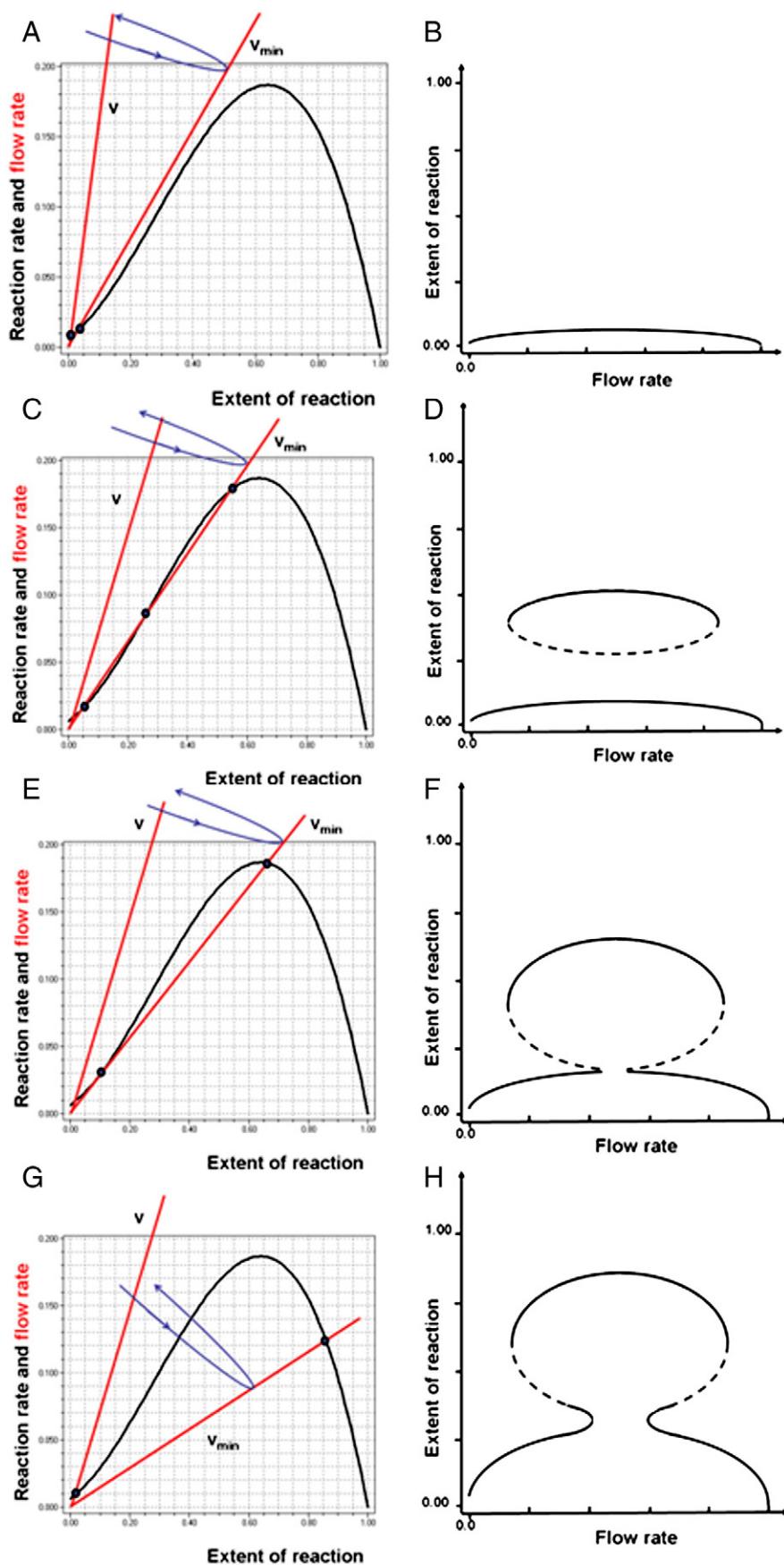


Fig. 6.7. Flow diagrams representing different stationary states for cubic autocatalysis with inflow and decay of B. (A) and (B) Single stable branch at low values of ξ . (C) and (D) Isola plus lower branch. (E) and (F) Transition from isola to mushroom. (G) and (H) Mushroom. Some unstable branches are shown dotted.

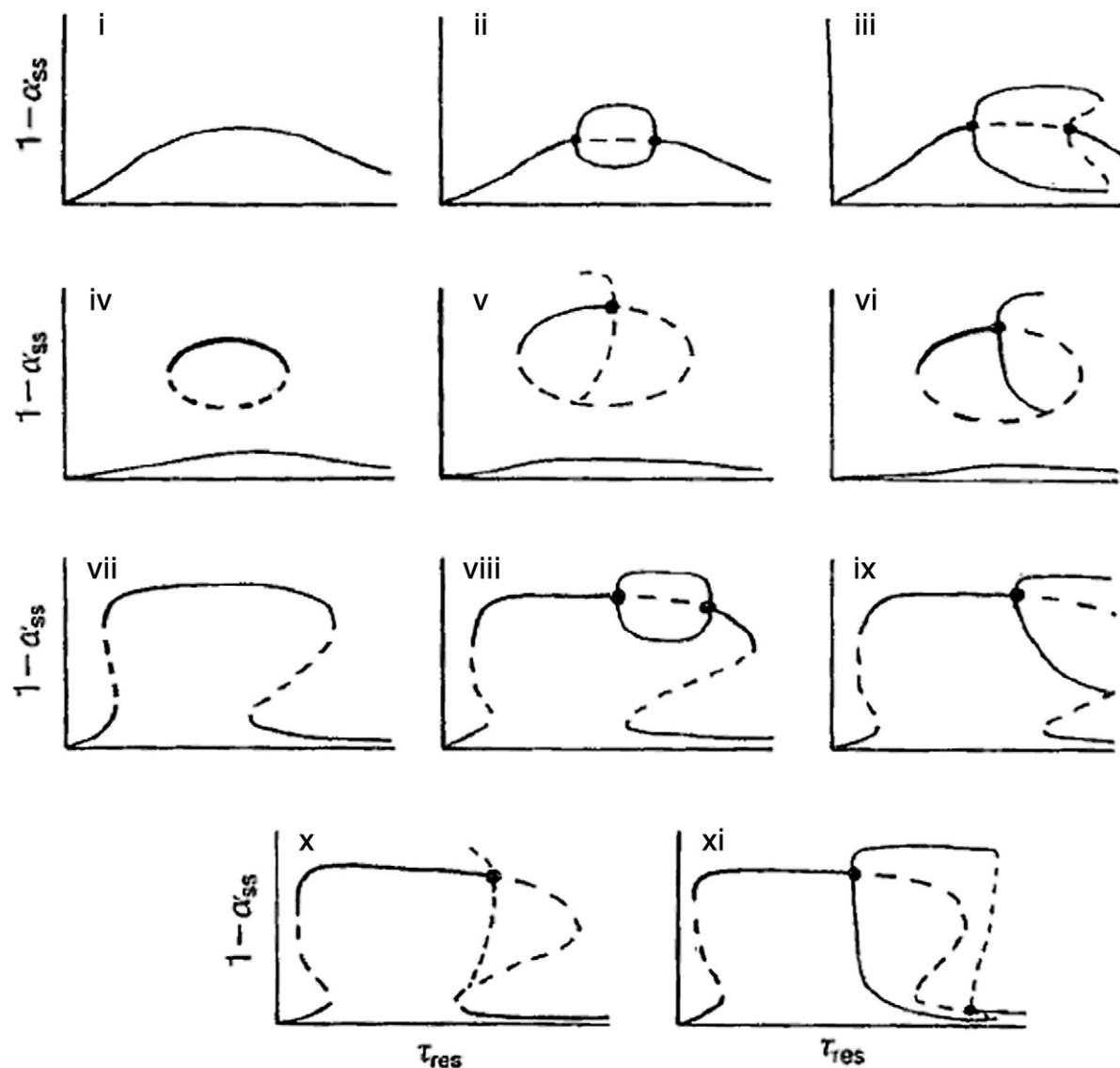


Fig. 6.8. Bifurcation diagrams for the cubic autocatalytic system with both A and B entering the system. Full lines are stable stationary states. Dotted lines are unstable stationary states. Full dots are Hopf bifurcations. Lines that emerge from a Hopf bifurcation indicate the extent and amplitude of oscillatory behaviour that emerges or dies at a Hopf bifurcation (After Gray and Scott, 1990).

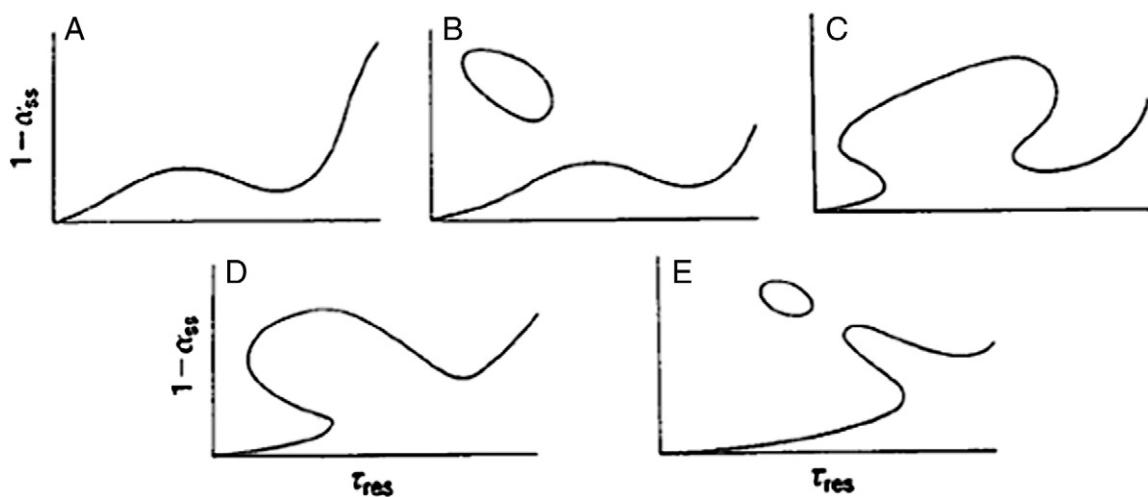


Fig. 6.9. Five stationary states developed for the system illustrated in Fig. 6.1(D). (A) Unique state. (B) Isola. (C) Mushroom. (D) Single hysteresis loop. (E) Single hysteresis loop plus an isola (After Gray and Scott, 1990).

cubic autocatalysis treated in previous sections however it turns out to be much more complicated (Uppal et al., 1974, 1976). Hints of this complexity are seen in Fig. 4.3(a) where the curve illustrating the reaction kinetics for this system is compared to those for quadratic and autocatalysis. The curves are superficially of the same form so we expect somewhat similar behaviour; it is the long incubation behaviour before rapid reaction rates ensue for the exothermic reaction that introduces greater complexity. This particular reaction is particularly relevant to mineralising systems since many oxidation reactions involving the reaction $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ – electron are exothermic.

Consider a first order chemical reaction that involves an intermediate step, so that A is converted to P and then P is converted to B with rate constants k_A and k_B as shown below:



We also assume that the reaction $\text{P} \xrightarrow{k_B} \text{B}$ is exothermic with a heat of reaction $\Delta H_B < 0$. The rate constant k_B obeys an Arrhenius temperature dependence:

$$k_A = k_A^0 \exp\left(\frac{-Q}{RT}\right) \quad (6.22)$$

where Q is the activation energy for the reaction, R is the gas constant and T is the local absolute temperature. As a first step we assume the rate constant for the reaction $\text{A} \xrightarrow{k_A} \text{P}$ is independent of temperature. We also assume the mixture is well mixed and sits in a heat bath that has a temperature T_0 . The equations for mass and heat balance are:

$$\frac{da}{dt} = -k_A a \quad (6.23)$$

$$\frac{dp}{dt} = k_A a - k_B p \quad (6.24)$$

$$(V\rho c_p) \frac{dT}{dt} = (-\Delta H_A V k_A p) - \Sigma \chi (T - T_0) \quad (6.25)$$

where V and ρ are the volume and density of the reacting mixture, c_p is the specific heat, Σ is the surface area of the system and χ the surface heat transfer coefficient. t is time. We take as the initial conditions, $a(t=0) = a_0$, $p(t=0) = 0$, $b(t=0) = 0$, and $T(t=0) = T_0$. Then the solution to Eq. (6.23) is

$$a(t) = a_0 \exp(-k_A t). \quad (6.26)$$

Substitution of Eq. (6.26) into Eq. (6.24) gives

$$\frac{dp}{dt} = k_A a_0 \exp(-k_A t) - k_B p. \quad (6.27)$$

We define $\Delta T = T - T_0$ so that Eq. (6.25) becomes

$$V\rho c_p \frac{d\Delta T}{dt} = (-\Delta H_A V k_A p) - \Sigma \chi \Delta T. \quad (6.28)$$

The solution to these equations is discussed by Gray and Scott (1990, Chapter 7). A diverse range of behaviour represented by flow diagrams is shown in Fig. 6.10 and again some of these states are stable, others unstable. Hopf bifurcations appear and are considered by Gray and Scott (1990, Chapter 7). Thus what at first sight would appear to be one of the simplest systems imaginable turns out to have an enormous range of complicated behaviours that depend on the residence time and hence on local fluctuations in permeability within a flow controlled system.

6.4. Parallel first order exothermic reactions in open flow systems

The behaviour of two parallel first order exothermic chemical reactions in a flow controlled system is discussed by Lynch et al. (1982). The system is shown diagrammatically in Fig. 6.1(f). The reactions involved are:



for which we define $Y = \frac{a}{a_0}$ and $Z = \frac{b}{b_0}$.

The two reactions are chemically uncoupled except for thermal feedback between the two. Since there are now more than three processes operating we expect chaotic behaviour and this indeed develops as shown in Fig. 6.11. Chemical concentrations oscillate chaotically with time together with the temperature. This is the kind of behaviour that one would expect in any hydrothermal system whilst the exothermic reactions responsible for the development of alteration are in progress. A summary of the behaviour of the systems represented in Fig. 6.1 is shown in Table 1.

6.5. Entropy production for nonlinear chemical systems

One of the primary goals of a thermodynamic approach to the formation of hydrothermal systems is to arrive at general principles that allow us to discuss the evolution of such systems without necessarily delving into the intimate details of the processes involved. One way of achieving this is to develop some over-arching entropy production principle that allows the stationary states of the system to be identified and defined in some detail. We review the progress in this field below.

The entropy production, \dot{s} , for any chemical reaction is given by Ross (2008):

$$\dot{s} = k \ln\left(\frac{r^+}{r^-}\right) (r^+ - r^-) \quad (6.29)$$

where r^+ and r^- are the forward and reverse rates for the reaction and k is Boltzmann's constant. If we take a simple chemical system given by

$$vA_{k_1^-} \rightleftharpoons^{k_1^+} vX \quad \text{and} \quad vX_{k_2^-} \rightleftharpoons^{k_2^+} vB \quad (6.30)$$

where v is a stoichiometric coefficient, then the stationary state for the production of X is given by

$$\frac{dx}{dt} = (k_1^+ a^v - k_1^- x^v) + (-k_2^+ x^v + k_2^- b^v) = 0. \quad (6.31)$$

If we now take $k_1^\pm = k_2^\pm = k$ then the stationary state concentration of X is

$$x^{ss} = \left\{ \frac{1}{2} [a^v + b^v] \right\}^{1/v}. \quad (6.32)$$

The variation of the entropy production about x^{ss} is

$$\delta\dot{s}(a, b, x^{ss}) = (\delta \ln x^{ss}) V k_B v k \frac{1}{2} [a^v + b^v] \ln \left\{ \frac{[a^v + b^v]^2}{4a^v b^v} \right\}. \quad (6.33)$$

We observe the algebraic identity that

$$\frac{[a^v + b^v]^2}{4a^v b^v} = \begin{cases} 1 & \text{for } a = b \\ > 1 & \text{for } a \neq b \end{cases} \quad (6.34)$$

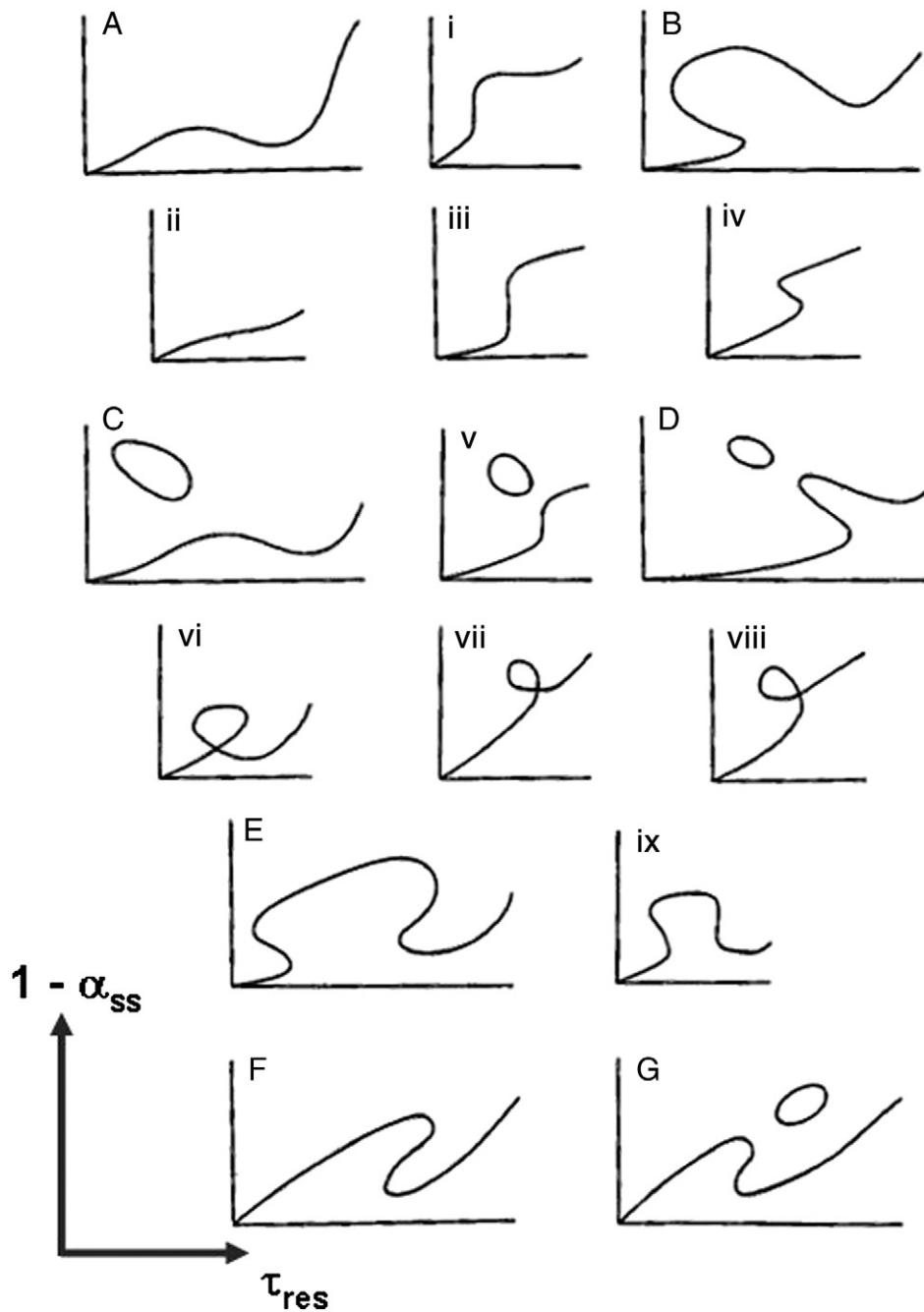


Fig. 6.10. Behaviour of a first order exothermal chemical reaction in a flow controlled system (After Gray and Scott, 1990).

and hence,

$$\frac{\delta s(a, b, x^{ss})}{\delta \ln x^{ss}} = \begin{cases} 0 & \text{for } a = b \\ > 0 & \text{for } a \neq b \end{cases}. \quad (6.35)$$

The condition $a = b$ corresponds to equilibrium whereas $a \neq b$ corresponds to a non-equilibrium stationary state. Hence the only extremum in entropy production corresponds to equilibrium. This argument is extended to the general case by Hunt et al. (1987, 1988), Ross (2008), Ross and Villaverde (2010), and Ross and Vlad (2005). Such results hold for isolated and diffusive systems where there are no flow constraints.

The general case for entropy production in an open flow reactor has not yet been examined but in the following we show examples

of entropy production in more complicated systems than that considered by Ross (2008). A general principle (quite different to that discussed by Ross) seems to emerge that the actual state adopted by the system corresponds to a state of maximum entropy production. In Fig. 6.12(a) we show plots of entropy production for an open flow system involving the cubic autocatalytic reaction $A + 2B \rightarrow 3B$ (Mansson, 1985). The figure shows a single oscillatory system where the entropy production oscillates with a fixed frequency. Plotted on this are both the mean entropy production for the oscillating system and the entropy production for the unstable stationary state prior to bifurcation. The constrained minimum entropy production principle picks the oscillatory state.

In Fig. 6.12(b) we show the Poincaré diagram for a coupled quadratic autocatalytic system, $A + X \rightarrow 2X$ and $A + Y \rightarrow 2Y$, that displays

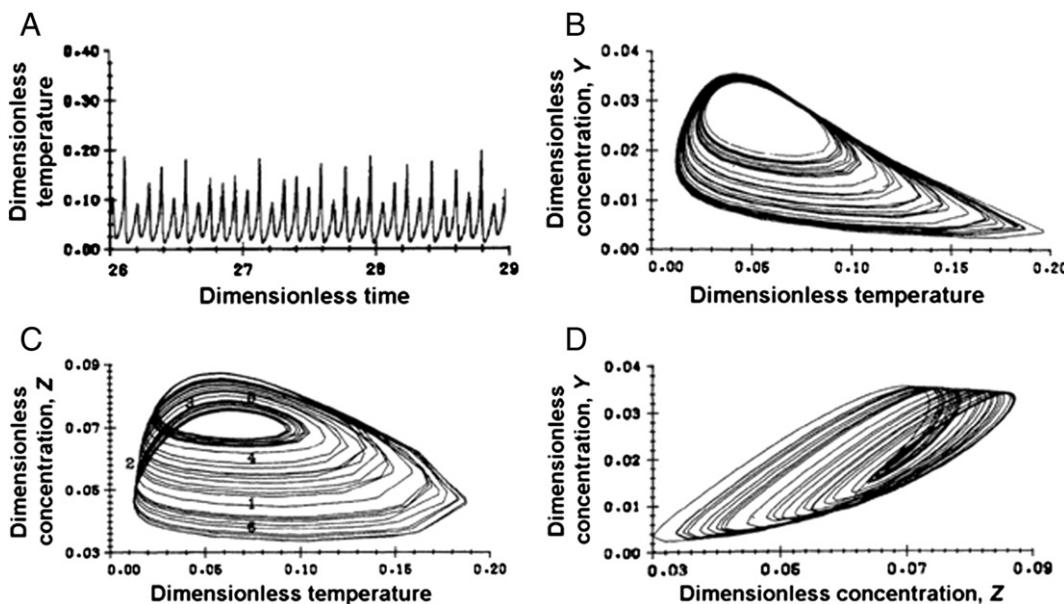


Fig. 6.11. Chaotic behaviour of two parallel first order exothermic reactions (after Lynch et al., 1982). (A) Dimensionless temperature plotted against time. (B) Dimensionless concentration Y plotted against dimensionless temperature. (C) Dimensionless concentration Z plotted against dimensionless temperature. (D) Dimensionless concentration Y plotted against dimensionless concentration, Z.

a period doubling sequence to chaos and with windows of period doubling within the chaotic regime (Lindgren and Mansson, 1986). Fig. 6.12(c) shows the entropy production for a small part of Fig. 6.12(b). The entropy production decreases progressively (and discontinuously at times) as one passes through this sequence but jumps to higher values within each of the period doubling windows in the chaotic regime. Fig. 6.12(d) shows an interpretation of Fig. 6.12(c), motivated by the work of Niven (2010a). The interpretation is that

the mode that is actually developed in the system and the transitions between modes are defined by a maximum entropy production principle whereas the actual stationary mode is defined by a modified minimum entropy production principle.

Mahara and Yamaguchi (2010a,b) calculate the entropy production for a Gray-Scott reaction in which spatial patterns form. Fig. 6.13 shows the calculated entropy production correlated with the spatial patterns. Again, a maximum entropy production principle picks the transition between different regimes of behaviour. Thus one can see that in chemical systems a maximum entropy production principle defines the *transitions* between modes of operation of the system (steady → bistable → oscillatory → chaotic) whereas a minimum entropy production principle defines the actual mode of operation (steady, bistable, oscillatory, or chaotic).

Diagrams such as Figs. 6.12(d) and 6.13 although drawn for entropy production are reminiscent of the bifurcation diagrams drawn for nonlinear elastic buckling of layers and commonly known as *Snakes and Ladders* systems (Knobloch, 2008). It would seem reasonable to explore the behaviour of nonlinear chemical flow systems by similar methods.

7. Autocatalysis and heterogeneous reactions

As we have seen, many processes are responsible for the development of multiple stationary states and of instabilities in these states in open flow systems (Fig. 4.4). Perhaps the most important of these processes involve instabilities in parallel and/or networked exothermal reactions, of which oxidation reactions are an important example. Reactions of this type have long been recognised in industrial applications (Liljenroth, 1918; Van Heerden, 1953). Two other particularly important processes are autocatalysis and heterogeneous reactions. Brantley et al. (2008) define *autocatalysts* as catalysts that are the product of a reaction. Autocatalysts that build up in concentration in a solution cause the rate of a reaction to increase with time. Heterogeneous reactions are reactions that occur at surfaces (Ertl, 2009; Lasaga, 1981).

The emphasis in the geoscience literature on equilibrium or local equilibrium states means that relatively little attention has been devoted to the molecular or atomic mechanisms involved in mineral

Table 1
Summary of behaviour of simple systems discussed in Section 6.

System	Behaviour
1. Closed isothermal Cubic catalysis	Limited oscillations of composition. System evolves to equilibrium. Fig. 6.2.
2. Closed exothermal First order kinetics	Limited oscillations of composition and temperature. System evolves to equilibrium. Gray and Scott (1990, Chapter 4).
3. Open isothermal Cubic catalysis No decay of B Input of A only	S-curve – One branch unstable–bistability. No oscillations possible. Figs. 6.3 and 6.4.
4. Open isothermal Cubic catalysis Decay of B Input of A only	Single isola together with $\xi = 0$ as stationary states. Bifurcation on upper branch. Lowest $\xi = 0$ branch stable. Lower branch of isola unstable. Part of upper branch unstable when system falls to the $\xi = 0$ branch. Fig. 6.5.
5. Open isothermal Cubic catalysis Decay of B Input of A and B	Many phase portraits possible at Hopf bifurcation (Fig. 6.6). Evolution from a single stable branch at a low ξ to a single lower branch with an isola through to mushrooms. Isolas always have Hopf bifurcation on their upper branch. Mushrooms may have one or two Hopf bifurcations on upper branch with others on lower branch Fig. 6.8.
6. Open exothermic First order kinetics Single reaction	Range of behaviour similar to model 5 but greater variety. Isolas, mushrooms and breaking waves exist. Fig. 6.10
7. Open exothermic First order kinetics Two parallel chemically uncoupled reactions	Chaotic. Fig. 6.11.

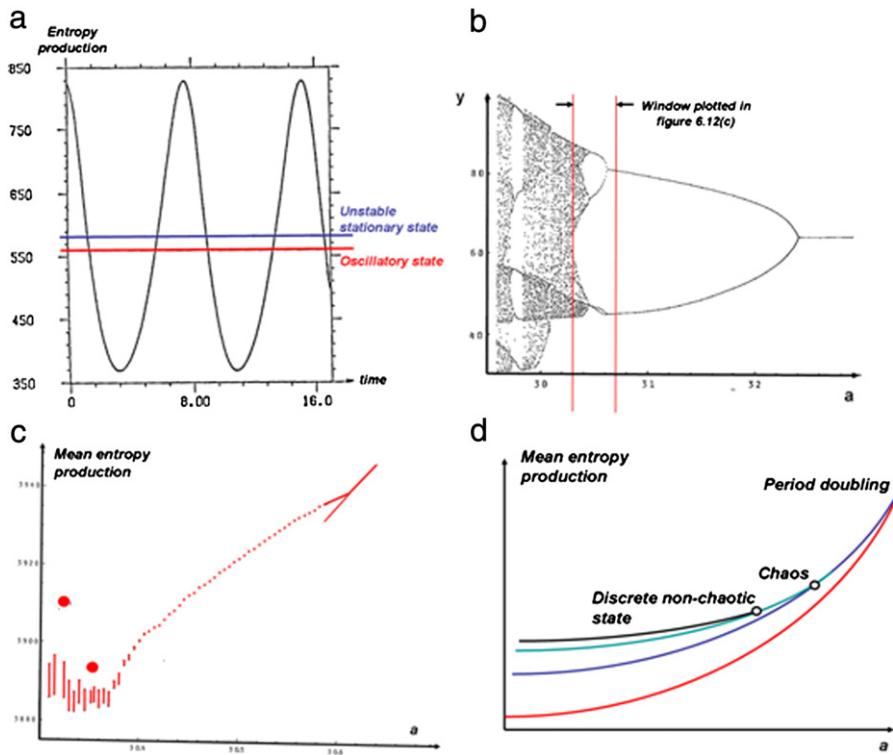


Fig. 6.12. Entropy production for oscillating and chaotic chemical reactions. (A) An open flow oscillatory cubic catalytic reaction. The mean entropy production is lower for the oscillatory reaction than for the unstable stationary state prior to bifurcation. A minimum entropy production rule picks the oscillatory state. After Mansson (1985). (B) Poincaré diagram for coupled quadratic autocatalytic reactions. After Lindgren and Mansson (1986). (C) The entropy production within the delineated window in figure (B). (D) An interpretation of (C) motivated by Niven (2010a). The proposal is that each state corresponding to simple stationary states, period doubling, chaos and isolated periodic windows within the chaotic regime possess individual entropy production distributions. The state that is selected corresponds to maximum entropy production.

reactions and hence there is relatively little data on mechanisms associated with the kinetics of processes involving mineral systems despite valiant efforts by authors such as Lasaga (1981, 1984). There is however a welcomed increasing emphasis on kinetics driven to some degree by the increasing use of modelling codes (Steefel and Maher, 2009) that take kinetics into account (Brantley, 2003; Brantley and White, 2009; Brantley et al., 2008; Brantley and Conrad, 2008; Dove and Han, 2007; Oelkers et al., 2009; Palandri and Kharaka, 2005; Putnis, 2009); see also other papers in Oelkers and Schott (2009). It is also important to recognise that many chemical processes in hydrothermal systems may rely on the presence of catalysts whether the actual process is autocatalytic or not (Carmichael, 1969). An example is the increasing awareness that gold can be an important catalyst (Bond and Thompson, 1999). We examine some aspects of autocatalytic and heterogeneous kinetic processes below.

7.1. Autocatalysis

We briefly review some experimental work on autocatalytic systems of interest in hydrothermal systems. Such experiments are difficult to perform especially at high temperatures and pressures and ideally one would like to see more attention devoted to molecular modelling of these systems. Such work is appearing (Gale et al., 2011; Kovacs and Lo, 2010; Plummer and Cowley, 2006; Skomurski et al., 2010; Zhu et al., 2005) but much more is needed in order to define the energetically most likely steps in mineral reactions.

Although there is a huge literature on the Fe(II)–Fe(III) system (most of which refers to closed systems) there appears to be relatively little published on the molecular mechanisms involved. Epstein et al. (1980), Lengyel et al. (1988), Orban and Epstein (1982), and Ottley et al. (1997) report on the oxidation of Fe^{2+}

by nitric acid. The systems are open to a flux of (NO). This is a homogeneous reaction in solution consisting of a series of seven steps and is autocatalytic in (NO). The reaction shows bistability (Orban and Epstein, 1982) and the development of travelling waves (Bazsa and Epstein, 1985; Pota et al., 1989). Although these experiments were conducted at room temperature there are clear indications of the influence of the exothermic nature of the reactions on the wave velocity. These experiments show that pattern development can occur during the oxidation of Fe^{2+} without autocatalysis in Fe but with a coupled autocatalytic intermediary (NO) instead. It would be of interest to model the homogeneous oxidation of Fe^{2+} at high temperatures to see if similar behaviour develops in aqueous environments where perhaps (OH) takes the place of (NO).

Experimental work on the oxidation of Fe^{2+} in oxidised aqueous solutions is reported by a number of authors, some of the literature being summarised by Houben (2004). Another relevant study is by Williamson and Rimstidt (1994). One conclusion is that the oxidation of Fe^{2+} is strongly accelerated at elevated pH. At least for near neutral pH conditions the reaction consists of a homogeneous reaction in solution plus a heterogeneous reaction at the solid interface (Tamura et al., 1976) described in total by:

$$-\frac{d[\text{Fe}^{2+}]}{dt} = k[\text{Fe}^{2+}] + k'[\text{Fe}^{2+}]_o [\text{Fe}^{2+}] - k'[\text{Fe}^{2+}]^2 \quad (7.1)$$

where $[\text{Fe}^{2+}]_o$ is the initial concentration of Fe^{2+} , $k' = k_s K / [\text{H}^+]$ and K is a constant given by $K = \frac{[\text{Fe}^{2+}]_{\text{adsorbed}} [\text{Fe(III)}]}{[\text{Fe}^{2+}] [\text{H}^+]}$. k and k' are the rate constants for the homogeneous and heterogeneous

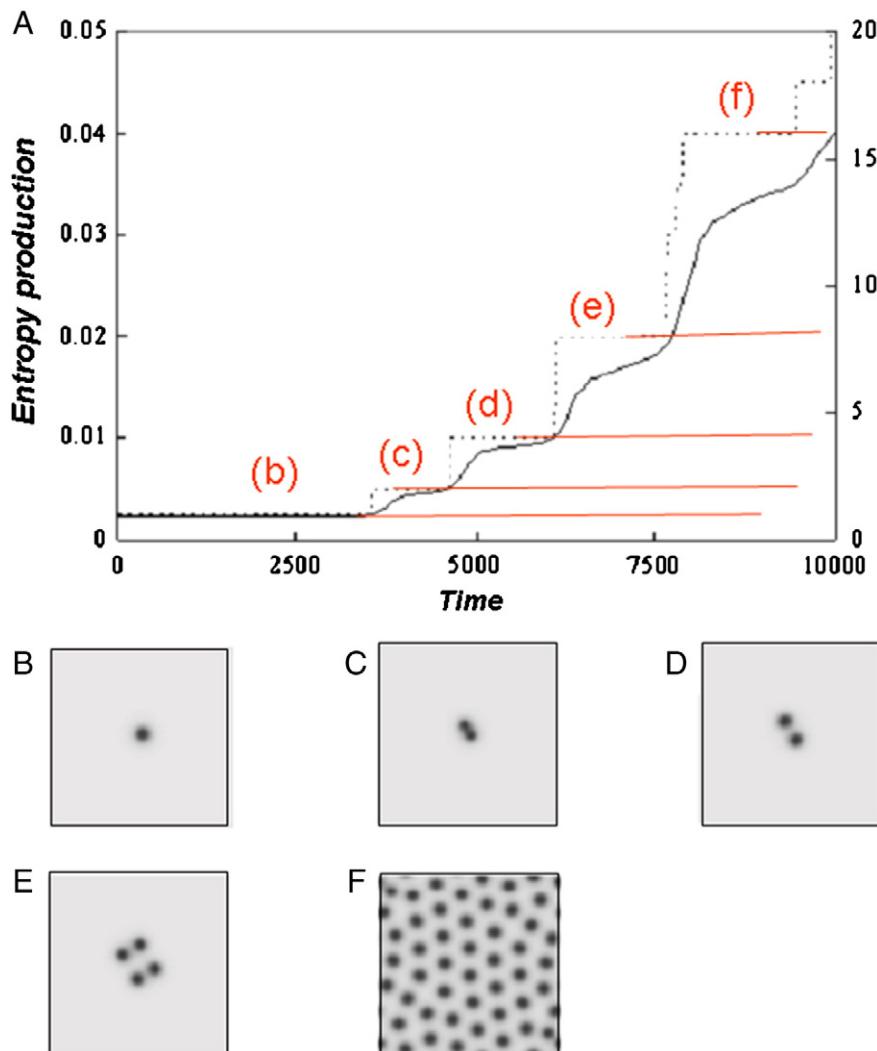


Fig. 6.13. Entropy production for a Scott–Gray reaction after [Mahara and Yamaguchi \(2010a,b\)](#). (A) Entropy production corresponding to the progressive formation of the different patterns shown in (B) to (F).

reactions respectively and $[Fe(III)]$ is the total concentration of Fe^{3+} expressed as $Fe(OH)_3$. Thus the production of $[Fe^{2+}]$ is autocatalytic in Fe^{2+} and dependent on pH. These experiments were conducted at room temperature. Other references to autocatalytic behaviour in the $Fe(II)$ – $Fe(III)$ system include Bligh and Waite (2010), Madden and Hochella (2005), Ottley et al. (1997), Pedersen et al. (2005), and Todd et al. (2003).

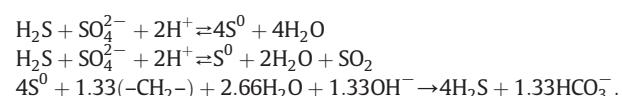
Another example of an autocatalyst is aqueous $Fe(III)$ that forms during oxidation of pyrite (Williamson and Rimstidt, 1994), and which then acts as an oxidant for the continued oxidation of pyrite in much the same way as $Fe(II)$ behaves in the experiments of Tamura et al. (1976). The mechanism of the oxidation of pyrite is complicated and varies according to species in solution, the nature of the intermediates, and the mechanism by which these intermediates produce the final product (Williamson and Rimstidt, 1994). The reaction for the oxidation of pyrite by ferric iron can be written as



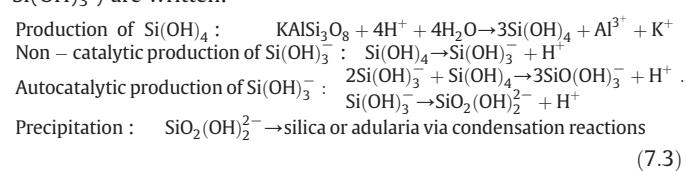
The measured rate of oxidation of pyrite in the presence of dissolved oxygen increases with increasing concentration of $Fe(III)$

so that the ferric ion acts as an autocatalyst. The reaction rate is also sensitive to pH.

Autocatalysis in other geologically relevant materials or processes has been proposed by Anderson et al. (1998a,b), Henley and Berger (2000), Machel (1987), Putnis (2002), Wang and Merino (1990, 1992), and Zhang et al. (2003a). The example from Machel (1987) involves redox sulphate–hydrocarbon reactions and autocatalytic production of H_2S . The reaction is written



The example from Henley and Berger (2000) is relevant to the common occurrence of oscillatory lamination of adularia and silica in epithermal veins. The reactions (which are cubic-autocatalytic in $Si(OH)_3^-$) are written:



These reactions have the same form as Eq. (6.2) and so Henley and Berger (2000) propose that this series of reactions behaves in the same way as the Brusselator (Fig. 6.2) but now the oscillations represent oscillations in the concentrations of adularia and quartz. Autocatalysis is perhaps more common in hydrothermal systems than is commonly appreciated. For instance the reaction system Eq. (1.1) is autocatalytic in H^+ .

Another example is the development of laminated quartz–carbon–chlorite veins in orogenic gold deposits (Adams, 1920; Cox, 1987; Thomas et al., 2011; Vearncombe, 1993; Wilson et al., 2009). Although there is some discussion as to whether or not the laminated structure (Figs. 7.1a and c) is due to incorporation of country rock between quartz veins we take the view that some examples could arise from unstable mineral reactions whereby layers of quartz are precipitated alternately with layers of chlorite/muscovite/graphite. The boundaries of these layers (Fig. 7.1B) are associated with increases in gold concentration along with other elements such as arsenic (Thomas et al., 2011).

Some of the possible reactions involved in the development of such structures are shown below.

1. Oxidation of pyrite:	$9FeS_2 + 18H^+ + 9H_2 \rightarrow 9Fe^{2+} + 18H_2S$
2. Alteration of K-spar to muscovite:	$3KAlSi_3O_8 + 2H^+ \rightarrow 2K^+ + KAl_3Si_3O_{10}(OH)_2 + 6SiO_2$
3. Dissolution of quartz:	$3SiO_2 + 3H_2O \rightarrow 3H_4SiO_4$
4. Muscovite to chlorite:	$2KAl_2Si_3O_{10}(OH)_2 + 3H_4SiO_4 + 9Fe^{2+} + 6Mg^{2+} + 18H_2O \rightarrow 3Mg_2Fe_3Al_2Si_3O_{10}(OH)_8 + 2K^+ + 28H^+$
5. Production of H^+ :	$CO_2 + H_2O \rightarrow HCO_3^- + H^+$
6. Production of carbon:	$CO_2 + 2H_2 \rightarrow C + 2H_2O$
7. Dissolution of ankerite:	$Ca(Fe, Mg)(CO_3)_2 + 4H^+ \rightarrow Ca^{2+} + (Mg^{2+}, Fe^{2+}) + 2CO_2 + 2H_2O$
8. Precipitation of gold:	$Au(HS)_2^- + 2H^+ \rightarrow Au^+ + 2H_2S$ $Au^+ + 0.5H_2 \rightarrow Au + H^+$

This set of reactions is greatly abbreviated; it lacks any reference to arsenic (Thomas et al., 2011) or to details of oscillatory quartz growth, catalysed by Al^{3+} and Fe^{3+} (Wang and Merino, 1990). The

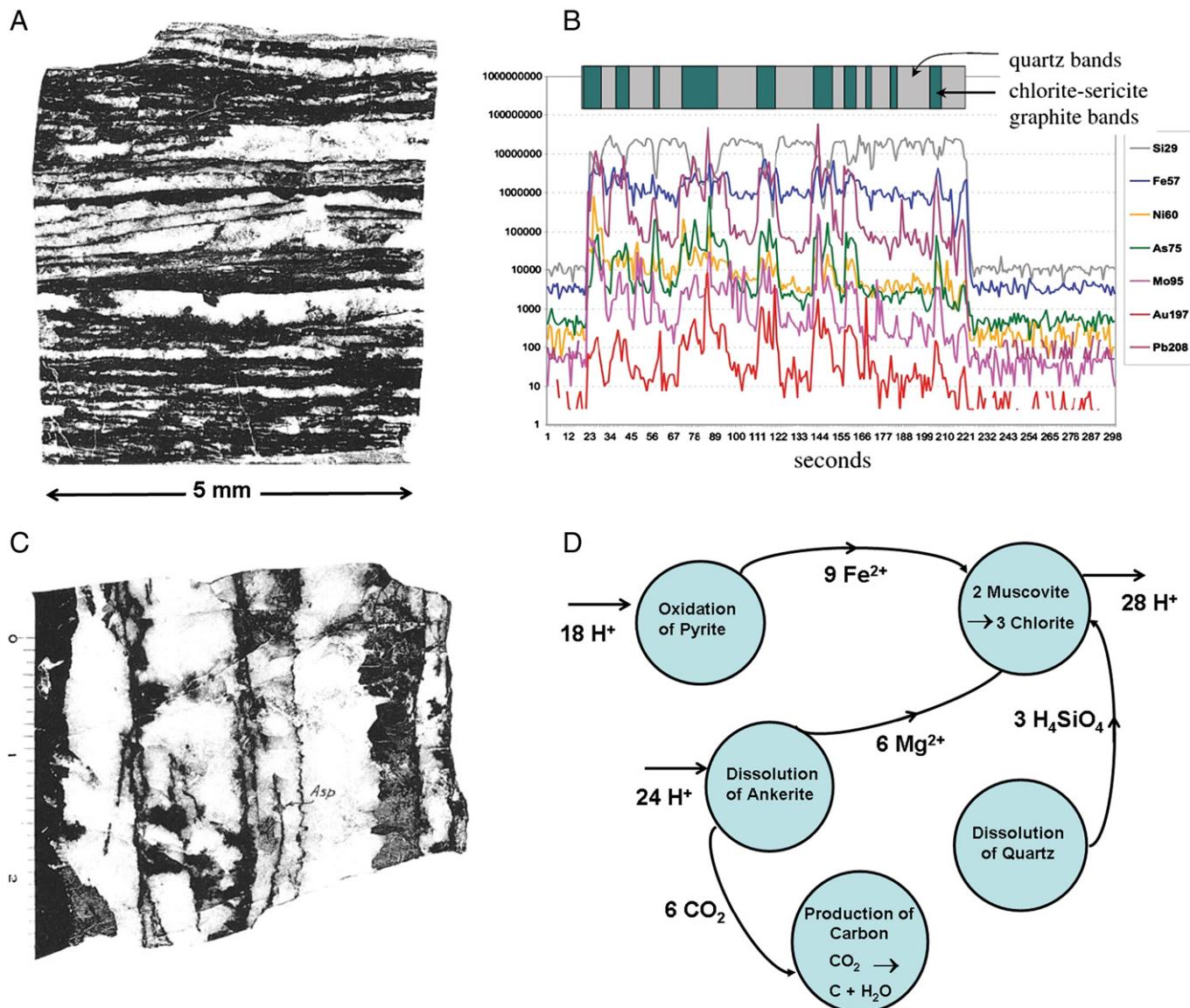
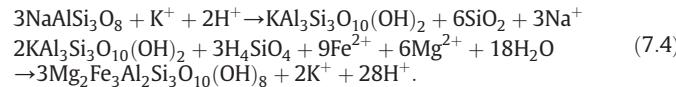


Fig. 7.1. Textures of laminated quartz veins. (A) Laminated quartz vein from Chace (1949). (B) Trace element scan across laminated quartz vein. From Thomas et al. (2011). (C) Laminated quartz vein with quartz dissolution. From Chace (1949). (D) Networked reaction diagram for the formation of chlorite in a laminated quartz vein.

reactions are shown in the form of a Carmichael (1969)-type diagram in Fig. 7.1(D) where it becomes apparent that both the reactions involving pyrite/muscovite/chlorite and ankerite/muscovite/chlorite are autocatalytic in H^+ with the potential for oscillations in banding as proposed for quartz/adularia by Henley and Berger (2000). These kinds of reactions need to be examined more closely with good petrographic and chemical work to establish the details of the networked reactions.

Yet another example is the common system albite \rightarrow sericite \rightarrow chlorite proposed by Large et al. (2001) which again is exothermal, autocatalytic in H^+ and also dissolves silica thus providing an opportunity for enhancing, or at least maintaining, the permeability:



7.2. Systems with heterogeneous kinetics

As indicated above the term heterogeneous kinetics refers to processes such as reaction, dissolution and precipitation that operate at the surface of a mineral grain (Dove and Han, 2007; Lasaga, 1981). Reviews of nonlinear behaviour are given by Ertl (2009), Imbihl and Ertl (1995), Libuda et al. (2005), Mizuno and Misono (1998), and Salciccioli et al. (2011). Kinetics associated with heterogeneous reactions commonly involve competition between processes operating at different sites on the surface of a grain. This may involve processes operating on different crystallographic planes or at steps on a particular crystallographic plane. Fig. 7.2 shows a common model for heterogeneous reactions, in this case for the gold (533) surface, where the surface is divided into parallel steps and troughs. The reaction kinetics are different depending on whether reaction occurs at a step or a trough and the different reactions can compete with each other.

7.2.1. Multiple stationary states arising from heterogeneous reactions

The development of multiple stationary states together with oscillatory behaviour and travelling waves is well documented in heterogeneous reactions (Ertl, 2009; Imbihl and Ertl, 1995, Libuda et al., 2005, Mizuno and Misono, 1998, Salciccioli et al., 2011). A general discussion of such behaviour is given by Ortoleva and Ross (1973, 1974). Detailed discussion of the effect of multiple reaction sites and of competition between sites and of different reactants for a particular site is given in Gray and Scott (1990) and part of that is repeated below.

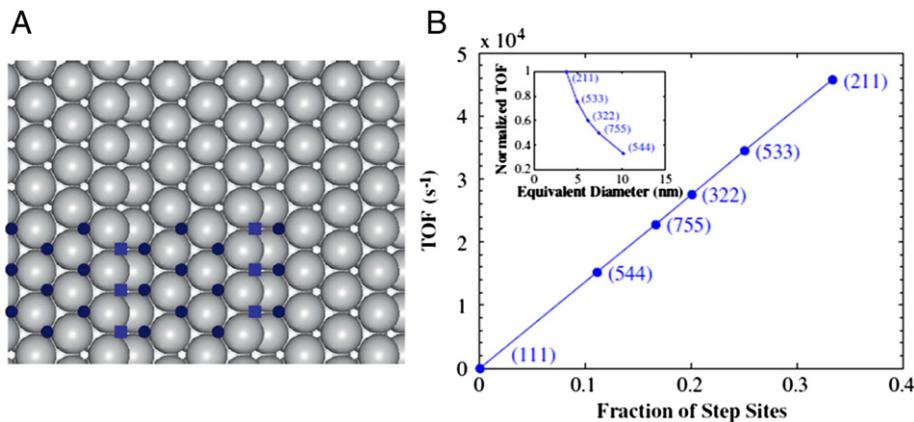


Fig. 7.2. Anisotropy of reaction sites for CO-oxidation reactions on gold particles. (A) Image of the (533) surface in the gold structure with "terrace" sites (which are sites in the rows of gold atoms comprising the (533) plane) marked as dark blue circles and "step" sites (which are sites on the edges of steps in these rows) marked as blue squares. (B) Plot of TOF (turnover frequency per monolayer) against the step site density for various crystallographic planes in gold. This means that the reactivity of the (111) plane which lacks step sites is negligible whilst that of the (211) plane is a maximum for reactivity of the planes plotted. Inset is a plot of the normalised TOF against the equivalent particle diameter of octahedral gold nanoparticles. From Salciccioli et al. (2011).

Specifically we deal with a situation where two reactants, P and R, compete for the same reaction site on a surface, S, a process that one would expect to be common in geological systems. If the reactions are written



and the total surface coverage is

$$\theta_S = (1 - \theta_P - \theta_R). \quad (7.6)$$

Then, the rate equations for the surface coverages θ_P and θ_R can be written

$$\begin{aligned} \frac{d\theta_P}{d\tau} &= p\theta_S - \kappa_1\theta_P - \theta_P\theta_R\theta_S^2 \\ \frac{d\theta_R}{d\tau} &= r\theta_S - \kappa_2\theta_R - \theta_P\theta_R\theta_S^2 \end{aligned} \quad (7.7)$$

where

$$p = \frac{k_1^+ P}{k_3}, r = \frac{k_2^+ R}{k_3}, \kappa_1 = \frac{k_1^-}{k_3}, \kappa_2 = \frac{k_2^-}{k_3}. \quad (7.8)$$

The behaviour of the system is easier to envisage in terms of a parameter, v , defined by

$$v = \theta_P\theta_R\theta_S^2 \quad (7.9)$$

and some results are given in Fig. 7.3. Again the system is highly nonlinear and shows a variety of responses depending on the values of v and r .

8. Discussion

In considering hydrothermal mineralising systems as evolving non-equilibrium flow systems the following points have been made in this paper:

- (i) Hydrothermal systems are open flow systems where mass and heat are fed into the reacting system and reacted, cooler fluids leave the system. The thermodynamics of such systems is different to the classical isolated and diffusive systems of metamorphic and metasomatic petrology where equilibrium is the

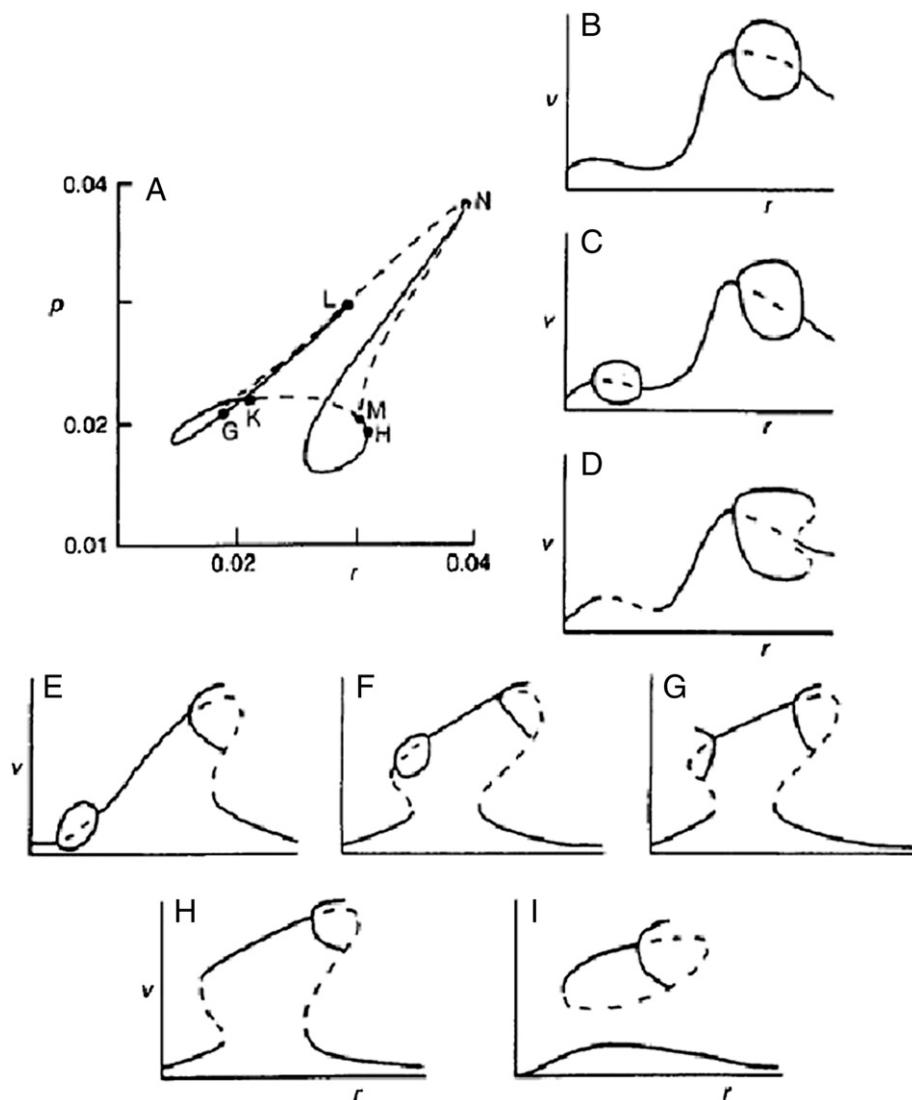


Fig. 7.3. Phase diagrams for heterogeneous reaction kinetics where two reactants compete for reaction sites on a surface. (A) Plot of p against r (defined in Eq. (7.5)). Full circles are Hopf bifurcations, full lines are stable stationary states and dotted lines are unstable stationary states. (B) to (I) Phase plots of v against r (defined in Eqs. (7.5) and (7.6)) for various sections across phase space. The representation is the same as Fig. 6.8. For details see Gray and Scott (1990). From Gray and Scott (1990).

eventual stationary state and the assumption of local equilibrium may be made for long residence times. In open flow systems the eventual state is one or more non-equilibrium stationary states and these states can be maintained far from equilibrium indefinitely so long as mass and heat continue to be added to the system and the relevant reactants in the system are not exhausted.

- (ii) There are two end-members of the spectrum of open flow systems. One is a *flow controlled system* where the inlet flow is held constant by a constant volumetric supply of fluid and the other is a *hydraulic-potential controlled system* where a gradient in hydraulic potential drives the flow. The first of these is represented by orogenic gold and IOCG deposits whilst the second is represented by MVT and Irish-style Pb/Zn deposits as modelled by Garven (1985) and Murphy et al. (2008). Hybrids between these end members exist and VMS and epithermal gold deposits are examples, the flow in these cases being controlled by fluid buoyancy superimposed on an imposed flow rate. It is important to distinguish between the two end member types of open flow systems because the first must adjust its local permeability (and hence porosity) to accommodate the

imposed fluid flux. Because of Darcy's Law this permeability adjustment depends on local fluctuations in imposed fluid flux and in fluid density and viscosity arising from chemical reactions and/or changes in temperature. A common mode of permeability adjustment in stressed rock is fracturing, veining, stockworks and brecciation. Both systems need to adjust their permeability to satisfy Darcy's law if a stationary state is to be maintained and this may also involve chemical precipitation and/or dissolution as chemical reactions proceed. Since a hydraulic potential controlled system simply shuts down if the permeability decreases to negligible values there is no mechanism to initiate brecciation and chemical dissolution processes become more important in such systems.

- (iii) In open flow systems even the simplest of uncoupled chemical reactions show a range of stable and unstable non-equilibrium stationary states. Coupling of more than two processes in such systems introduces the likelihood of chaotic chemical behaviour where the chemical composition and temperature fluctuate in time in a chaotic manner. Such processes include the operation of two chemically uncoupled reactions, both of which are exothermic, the operation of three chemically

- coupled (in the sense of Carmichael, 1969) isothermal reactions, autocatalysis in homogeneous reactions, competitive processes during heterogeneous reactions at surfaces, thermal-catalytic feedback on any of these processes, and chaotic mixing (Part II) induced by feedback of chemical reactions on fluid properties or by the flow geometry. The nature of the mode of behaviour (stable, unstable, bistable, oscillatory, chaotic) depends on many factors but an important parameter is the local porosity (and hence permeability). Thus the potential is for dramatically different behaviours in such systems in adjacent pieces of rock arising solely from fluctuations in permeability.
- (iv) The limited amount of work available indicates that an important selection rule for the mode of behaviour of the chemical part of the system may be a maximum entropy production rule. Such a rule seems to be able to pick non-oscillatory states from those associated with period doubling, chaos and windows of period doubling within the chaotic regime. There is as yet no rule for selecting the actual state but by analogy with other systems (Niven, 2009) a minimum entropy production rule may apply. Such a rule would be of a modified form of the extremum rule discussed by Ross (2008) who shows that for any *isolated* chemical system the only extremum for strict entropy production corresponds to an equilibrium state. For a flow controlled system it appears that the actual non-equilibrium state is picked by a minimum entropy production rule (which is different to that discussed by Ross, 2008). It is important to establish the entropy production rules that govern both the mode of operation and the stationary states for the chemical part of the system as this then allows us to track the evolution of the chemical part of the mineralising system using procedures developed by Niven and Andresen (2010). This is an important avenue for future work.
- (v) The observed order and systematics in mineral assemblages that characterise mineralised systems is not a sufficient condition to prove local equilibrium. The *excess work*, Γ , defined by Ross (2008) plays the same role in systems far from equilibrium as does the change in Gibbs energy, ΔG , for systems approaching equilibrium. Γ is the work necessary to displace a system from a non-equilibrium stationary state whereas ΔG is the work, other than the P-V work, necessary to displace a system from equilibrium at constant temperature and pressure. Since Γ is related to the chemical potential of a phase at steady state it is a function of the temperature as the system approaches steady state just as ΔG is a function of the temperature as a system approaches equilibrium. Both Γ and ΔG are Lyapunov functions; they approach non-equilibrium stationary states and equilibrium (respectively) in a smooth manner. For a system held far from equilibrium Γ drives the system to a non-equilibrium stationary state, is an extremum at all stationary states and $\frac{d\Gamma}{dt} \leq 0$ for relaxation to a stable stationary state; $\Gamma \geq 0$ for a displacement from a stationary state. The equivalent statements for a system approaching equilibrium are: ΔG drives the system to an equilibrium state, is an extremum at equilibrium and $\frac{d(\Delta G)}{dt} \geq 0$ for relaxation to an equilibrium state; $\Delta G \leq 0$ for a displacement from equilibrium. Thus one expects order in mineral assemblages characterising non-equilibrium stationary states just as for equilibrium states. In addition, the concept of excess work for a system approaching a stationary state enables a phase rule to be defined for such a system. Such a rule is of a similar form to the Korzhinskii phase rule for open systems so that fewer mineral phases are expected in an open flow system than in a closed system. This is an important line of future investigation.
- (vi) High chemical efficiency demands that efficient mixing of input fluids containing reactants occurs before the fluid mixture enters the control volume, or within the control volume before or as the chemical reactions proceed. However the fluid mixing process is not a passive process as would be the situation for mixing of two fluids of different colours. Mixing influences the nature of the chemical reactions taking place by exponentially increasing the surface area between reacting fluids and hence dramatically increases reaction rates. We discuss these processes in Part II.
- (vii) We have not devoted much space in this review to the complete solution of Eq. (2.9) where the diffusion process is coupled to the rates of production of chemical components by both reaction and advection. This is largely for lack of space since the topic is very large (Cross and Hohenberg, 1993; Epstein and Pojman, 1998; Fisher and Lasaga, 1981; Gray and Scott, 1990; Scott, 1994; Turing, 1952). Coupling with diffusion is capable of producing spatial patterning as is coupling with any process that advects or diffuses chemical components through the system. Deformation coupled to reaction plays the same role in developing spatial patterning (Ortoleva, 1994) as does fluid advection. At least at the millimetre to metre scale some spatial patterning of alteration and of mineralisation may arise from such coupling. The patterns can be stripes (layers), lineations or blobs (Bansagi et al., 2011). Such patterns at the kilometre scale are likely to result from reaction-advection coupling which is the subject of Part II. In particular Rusinov and Zhukov (2000, 2008) have modelled the development of banded wollastonite-hedenbergite skarns using a coupled reaction-advection model.
- (viii) As indicated above, in contrast to isolated and diffusive systems where the chemical reactions ultimately evolve to equilibrium under the imposed constraints, the chemical reactions in open flow systems evolve to one or more non-equilibrium stationary states. State selection is defined by the net flow rate and by the nature of the chaotic flow system during fluid mixing (Part II). Various processes result in nonlinear chemical kinetics in any chemical system but the influence of the net flow in defining the stationary state in open flow systems results in highly nonlinear chemical systems that have many modes of stationary state behaviour depending on local conditions. The net flow rate depends on the permeability and so slight local fluctuations in permeability can result in entirely different modes of chemical behaviour including little or no reaction, steady reaction at high yield (reaction extent), and oscillatory and chaotic behaviour at both high and low yields. Such strong dependence on local conditions also is apparent in spatial patterning. Oscillatory and chaotic behaviour are particularly important for mineralisation processes in well mixed systems. An example is where the mean environment is oxidised and acid with strong excursions into a reduced and alkaline environment. This leads to oscillatory or chaotic precipitation of sulphides and metals such as gold. The nonlinear dynamics of the system can produce spatial patterning where mean environments that are acid and oxidised are embedded in regions that are alkaline and reduced thus producing the strong gradients in Eh and pH observed in mineralising systems. This patterning is scale invariant and results from different phenomena operating at different scales but each producing the same range of nonlinear chemical behaviour at the relevant scale. Such processes include competitive reaction sites at crystal surfaces at the nanoscale, autocatalysis and thermal catalysis (especially in simple oxidation reactions) at intermediate scales and chaotic mixing at all scales including the km-scale (Part II).
- (ix) One goal of any analysis of the thermodynamics of a nonlinear system is to understand the rules, at a fairly general level, that describe the evolution of the system. This enables the precise evolution of complex systems such as mineralised

hydrothermal systems to be specified without introducing the details of the vast range of chemical and physical processes that operate within such systems. Such an approach has been spectacularly successful for the Earth's global weather system (Paltridge, 1975, 1978, 1981, 1981, 2001, Paltridge et al., 2007). In many systems these rules are expressed as statements of extrema in the entropy production that are rules for selection of both the operating modes of the system and for tracking the evolution of stationary states with changes in the control parameters of the system. The example given in Section 4.1.2 by Niven (2010b) is of a flow control system comprised of two parallel pipes. A maximum entropy production principle selects between the two operating modes of the system, laminar or turbulent flow, and a minimum entropy production principle allows one to identify stationary states for both modes and track their evolution with changes in control parameters.

In the case of hydrothermal systems, we need to identify what the operating modes might be. Perhaps there are only two modes, mineralised and unmineralised? Do these two modes correspond to exothermal-dominated operation (with the production of carbonates, iron oxides, OH-bearing minerals such as chlorite, muscovite, kaolinite, pyrophyllite) and endothermic-dominated operation (with the production of metals, sulphides, and anhydrous silicates)? If so, then it is easy to see how a maximum entropy (or heat) production rule may identify such a transition. Do giant mineralised hydrothermal systems pass through several of these mode-switches? The evidence seems to say definitely yes. For instance the inception of endothermic-dominated reactions could result in a slight decrease in temperature with an attendant increase in both the viscosity and density of the fluid in the system thus initiating brecciation. An increase in temperature decreases both the fluid viscosity and density and facilitates the flow of fluid at the current permeability. The evolution of giant hydrothermal system may be a progression through many exothermal–endothermic–exothermal transitions in the same way as efficiently combusting or explosive systems do (Law, 2006). A maximum entropy production rule would distinguish these transitions and enable them to be defined in terms of control parameters. For the same system each transition between modes probably represents an overall decrease in entropy production rate as the solid reactants in the system are exhausted. Then a minimum entropy production law would enable steady states to be identified and tracked. The overall system would resemble the evolution of the chaotic chemical system described in Section 6.5. By analogy with Section 6.5 we present Fig. 8.1 as one speculation on how a giant hydrothermal system might behave.

In order to follow the evolution of entropy production in a hydrothermal mineralising system the expression for the total entropy production needs to be developed in some detail. At a very general level this is (Hobbs et al., 2011):

$$T\dot{s} = \Phi = \Phi^{\text{def}} + \Phi^{\text{fluid}} + \Phi^{\text{heat}} + \Phi^{\text{chemical}} \geq 0. \quad (8.1)$$

To some extent Eq. (8.1) has been expanded by Niven (2009) for a flow controlled system but with solid deformation of the rock not specifically included. He shows that entropy extrema rules describe the evolution of such systems. The details of inclusion of solid deformation and chemical processes such as dissolution and precipitation are spelt out by Coussy (1995). The inclusion of solid deformation (that is, brecciation, fracturing and veining) and detailed chemical processes is not expected to change the broad conclusion of (Niven, 2009). We spell out one scenario for how entropy production may evolve below.

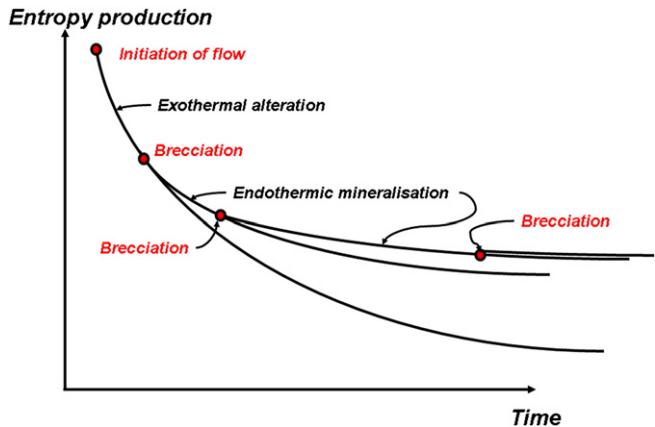


Fig. 8.1. A suggestion of how the entropy production might proceed during the evolution of a large mineralised hydrothermal system. The inception of flow and exothermal alteration represents the global maximum in entropy production. A switch in the mode of operation is initiated by a decrease in temperature of the fluid perhaps caused by waning of the alteration reactions arising from exhaustion of reactants such as K-feldspar. This initiates brecciation and the beginning of endothermic reactions such as those associated with mineralisation. Although the entropy production of the system continues to decrease the mineralising event represents a higher entropy production than would have been possible with exothermal alteration alone. Such a switch in modes can be repeated as the density and/or viscosity of the fluid evolves. As in chemical systems the switch in entropy production can be discontinuous.

8.1. Stage I: exothermal alteration

Φ is dominated by $\Phi^{\text{fluid}} + \Phi^{\text{heat}} + \Phi^{\text{chemical}}$. This stage may need to accommodate \dot{V} by an initial transient fracturing stage but once steady state is reached the system is dominated by Φ^{chemical} with heat production positive. If anything the temperature may increase in this stage resulting in lower μ and ρ^{fluid} ; K , ϕ are maintained by chemical dissolution and precipitation and are enhanced by the negative ΔV associated with many of these reactions (Haack and Zimmermann, 1996; Norton and Cathles, 1979). This stage lasts until the reactant (such as K-feldspar) in the control volume is depleted.

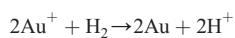
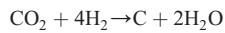
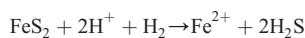
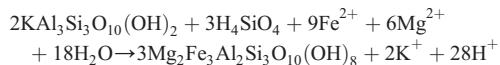
8.2. Stage II

As the exothermal stage I ends, the temperature drops and μ and ρ increase. In order to accommodate \dot{V} , K must increase by fracturing (veining) and/or brecciation. This stage is exothermal if there is sliding on the new surfaces and can drive endothermic reactions. Steady state is achieved at constant T when $\Phi^{\text{def}} = \Phi^{\text{chemical}}$ and the heat generated by deformation balances that needed to drive the endothermic reactions. If Φ^{chemical} becomes greater than Φ^{def} the temperature drops, μ and ρ increase and fracturing increases until $\Phi^{\text{def}} = \Phi^{\text{chemical}}$. If Φ^{def} becomes greater than Φ^{chemical} the temperature rises and drives more Φ^{chemical} until steady state is achieved again. This stage lasts until there is a significant change in imposed fluid flux or a change in the temperature and/or chemistry of the imposed fluid.

8.3. Stage III and further stages

A new stage in the system can only arise if a new exothermal phase is initiated. If the system must still continue to accommodate \dot{V} after Stage II wains then it can only do so by brecciation and this may initiate a new phase of endothermic chemical reactions if the reactants are available to do so. An example is the reaction sericite \rightarrow chlorite given in Eq. (7.4) (Large et al., 2001). Once the initial set of exothermal reactions is complete the evidence from observations on ore systems is that competing exothermal and endothermic reactions take place in the form of overlapping formation of

hydrous phases, carbonates and/or iron oxides with phases such as sulphides such as pyrite, arsenopyrite and gold. In fact this sequence of events is autocatalytic in H^+ as is illustrated by the reactions:



so that exothermic and endothermic reactions operate together to consume or produce H^+ . Notice that since these reactions are autocatalytic in H^+ they are expected to be unstable and oscillate in time and space.

The system may oscillate through stages II and III for extended periods. Finally the system shuts down because \dot{V} decreases below a level where a relevant stationary state can be accessed.

Stage III may be initiated by an increase in H^+ for instance or by an increase in the density and viscosity of the incoming fluid due to cooling of the fluid or an increase in NaCl content as is perhaps the case for Olympic Dam (Oreskes and Einaudi, 1990) or fluid-gas composition as for some Yilgarn gold deposits (Neumayr et al., 2005). Failed hydrothermal systems never get past Stage I. Really large systems continue to operate driven by continued influx of fluid and oscillate many times through Stages II and III. The size of the system, and whether it is highly mineralised or not, is not just because the flux of fluid is large, and continues over a long time. The fundamental issue is that the rock mass must evolve with time in order to initiate different stages of development that are expressed in the rock mass by new phases of fracturing, veining or brecciation, localisation of fracturing and/or brecciation, and new elements of the paragenetic sequence that must compete with each other to use H^+ and keep the permeability sufficient to accommodate the imposed flow.

An important aspect of the evolution of the system is that expressed by Niven (2009) regarding competition between sub-control units in evolutionary stages that involve the maintenance of permeability (either by fracturing or chemical processes). Entropy production drives the development of structure and function and organisation. Since fluid flow is strongly focussed into the most permeable units leaving less permeable regions barren of fluid (Phillips, 1991; Zhao et al., 2008, Chapters 6–8), if a subunit (such as is illustrated in Fig. 2.1b) does not maintain its permeability the local flow is diverted to ones that do and that subunit is starved of fluid. Moreover subunits downstream from the "failed" subunit also are starved whilst subunits downstream from the "successful" subunit now need to maintain their permeability. Thus pathways for fluid flow and hence for chemical reaction are both organised and localised. Moreover they are transient and can be diverted to new systems of flow and reaction if one subunit fails to maintain permeability. As indicated above, an important step in large mineralised systems seems to be the localisation of high permeability zones. This in turn has an influence on the types of chemical reactions that operate and the nature of their stationary states. Localisation of high permeability networks within the previously altered system may be the significant event that leads to the subsequent operation of the mineralising

phase. It is emphasised that this competitive phase of hydrothermal system evolution applies not only to the "plumbing system" as described above but to all processes that operate in the system (Niven, 2009, 2010a). An example is the competition between exothermic and endothermic mineral reactions.

Future work involving the detailed analysis of entropy production and its evolution with time in hydrothermal mineralising systems holds the promise of a precise description of the non-equilibrium stationary states that delineate mineralised from non-mineralised systems and the size and grade of systems without the need for enormous detail regarding the precise chemical and physical processes operating within the system. As an example of how this might be carried out we first briefly refer to how this has been achieved for the Earth's climate (Paltridge, 1975, 1978, 2001). The arguments are summarised in Fig. 8.2. The Paltridge "two box" model of the Earth's climate is shown in Fig. 8.2(A) and the arguments involved have been summarised by Kleidon (2010) and Lorenz (2010). Both the equatorial and polar regions of the Earth receive radiative heat from the Sun with greater intensity at the equator than at the poles. Heat is radiated into space but the gradient in temperature between the equator and the poles drives mass transport in the atmosphere and this is expressed as the climate of the Earth. Paltridge proposed that this temperature gradient is such as to maximise the entropy production of the system. This rather simple model is sufficient to explain the temperature and cloud distribution on Earth. The simplicity of the model contrasts with the elaborate computer models that occupy the time on many supercomputers on Earth incorporating intricate details *inter alia* of atmospheric and oceanic chemical reactions, ocean-atmosphere interactions and convective motions in the atmosphere.

Fig. 8.2(B) shows a "three box" model of a flow controlled hydrothermal system inspired by the Paltridge model. Fluxes of heat and mass are added to the system from mantle and/or crustal sources and leave the system somewhere in the crust. Within the

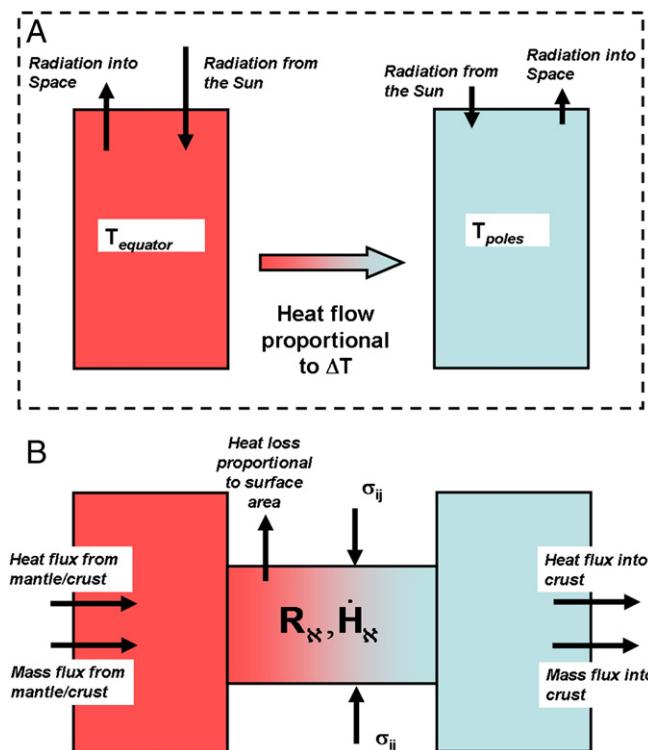


Fig. 8.2. Models of systems where entropy production principles apply. (A) The Earth's climate system. The gradient in temperature between the equatorial and polar regions is such as to maximise entropy production. See text for discussion. (B) A three box model of a flow controlled hydrothermal system. We need entropy production principles for this model that will define conditions for maximum size and grade of the mineralisation and for the modes of operation of the reactor system.

hydrothermal system, which is subjected to a stress, σ_{ij} , n coupled reactions take place with rates, R_k , each producing heat at rates, H_k . Extremum entropy arguments say that the nature of the chemical reactions occurring within the system is such as to maximise the entropy production rate. Further, the arguments of Niven (2009, 2010a) indicate that, since this is a flow controlled system, the nature of the steady states adopted by the system are identified by a minimum entropy production principle. The reactions that need to be considered are the dominant ones that control Eh, pH and heat production/consumption; an assumption needs to be made that many other reactions are "slaved" to these dominant reactions. Thus the system is reduced to the minimum number of mechanisms that are necessary and sufficient to describe the evolution of the system. There is no need to incorporate the intricate detail of all the hydraulic, mechanical and chemical processes that operate. The entropy production for this flow controlled system is given by an expansion (see Coussy, 1995, Chapter 3; Niven, 2009, 2010a) of the second law of thermodynamics Eq. (8.1):

$$\begin{aligned} \dot{s} = & \frac{1}{T} \sigma : \dot{\epsilon}^{\text{plastic}} [\text{dissipation due to solid deformation}] \\ & + \tau : \nabla \left(\frac{V}{T} \right)^T [\text{dissipation due to fluid deformation}] \quad (8.2) \\ & - \sum_k \frac{1}{T} \left[\dot{\xi}_k A_k + \dot{H}_k \right] [\text{chemical dissipation}] \\ & - \sum_N \mathbf{j}_N \cdot \left[\left(\frac{\mu_N}{m_N T} \right) - \frac{\mathbf{g}}{T} \right] [\text{dissipation due to fluid flow across chemical gradients}] \\ & - \mathbf{j}_H \cdot \nabla \left(\frac{1}{T} \right) [\text{dissipation due to heat conduction}] \\ & \geq 0 \end{aligned}$$

where in this case \dot{s} is the local entropy production for an element of the system per unit volume, $\sigma, \dot{\epsilon}^{\text{plastic}}$ are the stress on the solid matrix and the plastic strain rate of the solid matrix arising from fracturing and any other modes of permanent deformation, τ is the shear stress on the fluid, V is the velocity of the fluid, there are n chemical reactions of interest and N chemical components, $\dot{\xi}_k$ and A_k are the reaction rate and affinity for the k th chemical reaction, \mathbf{j}_N is the flux of the N th chemical component and μ_N, m_N are the chemical potential and molar mass of the N th chemical component, \mathbf{j}_H is the heat flux, \mathbf{g} is the acceleration due to gravity, ∇ is the gradient operator, \cdot represents the scalar product of two vectors, $:$ represents the scalar product of two second order tensors and superscript T is the transpose of a matrix. Eq. (8.2) has to be maximised subject to the constraints of fluid and mass transport into and out of the system. Examples are given by Coussy (1995) and Niven (2009). This is the subject of present work. However already some insight is gained from Fig. 8.2(B) in that the heat loss from the system into the surrounding rocks is proportional to the surface area, Σ , of the system so that as the volume, V , of the system becomes larger, the ratio Σ/V becomes smaller. Thus optimisation of this ratio controls some of the heat loss from the system and hence has a bearing on the optimal size of the system.

From the point of view of a mineral explorer this review suggests that a failed hydrothermal system is characterised by widespread exothermal alteration comprised of hydrous silicates, carbonates and iron oxides but with no evolution past that stage. The feature that indicates that a system is becoming productive is that fracturing, veining, brecciation and/or stockworks begin to overprint the earlier alteration. The signal that says that the system has evolved into a mineralised system is widespread evidence of competitive processes that involve exothermal processes such as fracturing (in its many forms), localisation of fractured networks and the formation of hydrous phases (particularly chlorite or biotite), carbonates and iron oxides in competition with endothermic processes such as the formation of sulphides and anhydrous silicates. The

competitive phase may go through many overprinting cycles. This mode characterised by competition is autocatalytic in H^+ ; autocatalytic behaviour in networked chemical reactions is itself a competitive process. This competitive environment in a non-equilibrium system is the signal that the system has been successful as a mineralising system and that the environment is sufficient to produce metals such as gold and metal bearing sulphides. In Part II we elaborate upon this evolutionary process for hydrothermal systems by concentrating on the critical plumbing systems necessary to efficiently premix fluids before they enter the hydrothermal reactor or how fluids can efficiently mix within the reactor. This mixing process produces its own set of characteristic behaviours that are scale dependant.

9. Concluding remarks

This paper reviews some of the principles that govern the operation of hydrothermal systems viewed as open flow chemical reactors. The evolution of these systems is quite different to that of isolated or diffusive systems classically used in metamorphic and metasomatic petrology in that open flow systems evolve to one or more non-equilibrium stationary states whereas the classical systems evolve to equilibrium. A particular stationary state can be maintained far from equilibrium indefinitely as long as the required nutrients continue to be fed to the system and as long as necessary reactants within the system are not exhausted. We have concentrated here on flow controlled reactors rather than hydraulic-potential controlled reactors. Flow controlled reactors constitute mineralising systems such as orogenic gold and IOCG systems whilst hydraulic-potential controlled systems constitute MVT and Irish style Pb/Zn deposits. Flow controlled reactors must switch to a new stationary state once one stationary state is terminated in order to continue to accommodate the imposed flow conditions. In many flow controlled mineralising systems such a switch is represented by a transition from regional carbonate/hydrous silicate alteration systems that are basically exothermic to a competition between the processes of fracturing/veining/brecciation (exothermic) which achieves the required permeability and sulphide/silicate deposition (endothermic) which destroys the permeability and extracts heat from the system. Many cycles of this latter competitive stage (which is autocatalytic in H^+) may occur in order to continuously accommodate the imposed flow. The chemical reaction rates and the stationary states of the chemical reactions within a flow controlled system are controlled by the imposed flow but the presence of multiple stationary states in most if not all natural chemical systems means that the local chemical processes are very sensitive to the local flow which is controlled by the local permeability. Thus in the one small piece of rock many modes of chemical behaviour, including no reaction, steady reaction, oscillatory and chaotic reaction modes, may occur depending on local fluctuations in permeability. Oscillatory and chaotic modes are fundamental in producing mineralisation. A particular part of the rock mass may oscillate both temporally and spatially in Eh and/or pH such that its average state is perhaps oxidised and acid with periodic or chaotic excursions into reduced and more alkaline conditions with the accompanied precipitation of sulphides, metals such as gold, and carbon. Again this represents a competition between exothermic behaviour (oxidation, hydration, dissolution of silicates) and endothermic behaviour (precipitation of sulphides, silicates and metals).

Open flow reactor systems are governed by principles involving extrema in entropy production. Thus flow controlled systems operate under conditions that locally maximise the entropy production. These conditions comprise the mode of operation of the system (steady, bistable, oscillatory, chaotic-chemical reaction systems; fracturing). The precise form of the non-equilibrium stationary state (the chemical reactions that operate, whether they are competitive or not, whether the fracturing stage involves brecciation, stockwork formation and/or sliding on fractures) is governed by a minimum entropy

production principle (Niven, 2009, 2010a). These principles, once explored in detail, will enable modelling of hydrothermal systems with a minimum of detail of the processes involved. Certainly the demand for each local unit in the system to operate at maximum entropy production drives cooperative action between units because those that achieve maximum entropy production attract the available flux of material and continue to evolve at the expense of those that do not achieve maximum entropy production and drop to zero or low chemical reaction efficiency. This competitive process leads to localisation of the permeability (in the form of localised fracture zones or brecciation) and such localisation then has an impact on the type of mineral reactions that operate and the nature of their stationary states. Such localisation within the complete alteration system seems to be a fundamental step in producing large high grade flow controlled deposits. In posing these operating principles it is important to appreciate that the arguments apply only to the *control volume*. Far field effects such as changes in the fluid producing system that influence heat and fluid flow into the control volume are not part of these arguments. Such effects clearly influence the evolution and gross behaviour of the control volume and if they are critical elements of the system then the control volume needs to be expanded in spatial scale to include them. Such models are more on the crustal or lithospheric scale than the ore body scale and are beyond the scope of this review.

We see then that the characteristics of hydrothermal mineralising systems derive essentially from the fact that such systems constitute open flow systems rather than the classical isolated or diffusive systems. These systems are nucleated by the addition of H^+ from an external source to a reactive rock mass resulting in a system of exothermal alteration reactions. This stage evolves into a fractured system and then to a system where mineral reactions autocatalytic in H^+ produce a competitive environment that allows mineralisation to develop. The driver for this evolution is a flux of fluid and heat. Hydrothermal systems operate at one or more non-equilibrium stationary states which are strongly influenced by the local permeability and switch between stationary states. They operate as non-linear chemical systems with multiple stationary states that are selected by details of the flow system. The multifractal nature and spatial scale invariance is a direct outcome of these characteristics.

This paper and its sequel provide a new approach (for the geosciences) that we hope will stimulate new ways to study the dynamics of ore systems. The approach demands a new generation of experiments and modelling and the design of ways of testing the processes discussed. It also requires that, in documenting relationships in ore systems, geologists and geochemists move away from the equilibrium view of such systems and examine mineral textures and overprinting relationships more carefully in the light of non-equilibrium thermodynamics and nonlinear dynamics.

In conclusion, to emphasise the importance of competitive processes in ensuring the longevity of a hydrothermal system, we paraphrase the classical conclusion reached by Schrodinger (see Niven, 2010a for further elaboration, Schrodinger, 1944, p71) with respect to the nature of life:

...a living hydrothermal system continually increases its entropy... and thus tends to approach the dangerous state of maximum entropy, which is death. It can only keep aloof from it, i.e. alive, by continually drawing from its environment negative entropy....What a hydrothermal system feeds upon is negative entropy.

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Appendix A

Table A1
Symbols used in the text with units.

Quantity	Description	Units
κ	Number of chemical species	Dimensionless
\mathcal{A}	Affinity; "driving force", of a reaction	$J \text{ kg}^{-1}$
A, B, C, \dots etc.	Chemical components A, B and C.... etc.	Dimensionless
B	A constant	s^{-1}
a, b, c	Concentrations of chemical components A, B and C	Dimensionless or mol kg^{-3} or moles/unit volume of fluid
a_0, b_0	Initial concentrations of A and B	Dimensionless or mol kg^{-3} or mol/unit volume of fluid
c_p	Specific heat capacity	$J/(kg K)$
c_i	Concentration of the i^{th} chemical species in solution	Dimensionless or mol kg^{-3} or moles/unit volume of fluid
D	Mass diffusivity	$m^2 s^{-1}$
D	Matrix of diffusive transport coefficients	$m^2 s^{-1}$
D_i	Diffusion coefficient	$m^2 s^{-1}$
D	Fractal dimension	Dimensionless
D_u	Fractal dimension of the unstable manifold	Dimensionless
D_{eff}	Effective fractal dimension	Dimensionless
D_a	Damköhler number	Dimensionless
D_g	Tensorial hydrodynamic dispersivity	$m^2 s$
E^K	Activation energy of the K^{th} reaction	$J \text{ mol}^{-1}$
\hat{e}	Unit vector along the stable manifold direction	Dimensionless
$F_k^{\text{in}}, F_k^{\text{out}}$	Volumetric flows of f_k into and out of the control volume	$m^3 s^{-1}$
f	Net flow rate	$\text{mol m}^{-2} s^{-1}$
f_k	An extensive variable	Depends on variable
f	degrees of freedom	dimensionless
g, g	Acceleration due to gravity; vector, magnitude	$m^2 s^{-1}$
\mathcal{H}	Hydraulic potential	Pa
\mathbf{J}	Sum of the fluxes	$\text{mol}/(m^2 s)$
K	permeability	m^2
k_T	Thermal conductivity	$W/(m K)$
k	Rate constant	Depends on chemical reaction involved
$k^+; k^-$	Forward and reverse rate constants for a chemical reaction	s^{-1} but depends on the reaction
$r^+; r^-$	Forward and reverse reaction rate for a chemical reaction	mol s^{-1}
k	Boltzmann constant	$J K^{-1}$
L	Characteristic length	m
$N(\varepsilon)$	Number of boxes required to cover the stable manifold	Dimensionless
n_k	Number of moles of the k^{th} chemical component	Dimensionless
p	Pressure	Pa
$p^{\text{fluid}}, \hat{p}$	Fluid pressure	Pa
q	Volumetric flow	$m^3 s^{-1}$
Q	Activation energy	$J \text{ mol}^{-1}$
R	Gas constant	$J K^{-1} \text{ mol}^{-1}$
R_i	Total reaction rate for reaction involving the i^{th} chemical species	$\text{mol}/(\text{kg}^3 \cdot \text{s})$
$R_i^{\text{homogeneous}}$	Reaction rates for homogeneous	$\text{mol}/(\text{kg}^3 \cdot \text{s})$
$R_i^{\text{heterogeneous}}$	and heterogeneous reactions	
S	A reacting surface	$m^2 \text{ m}^{-3} \text{ mol}^{-1}$

(continued on next page)

Table A1 (continued)

Quantity	Description	Units
S_{fluid}	Rate of production of fluid	mol s^{-1}
s	Specific entropy	$\text{J kg}^{-1} \text{K}^{-1}$
\hat{s}	Unit vector along the stable manifold direction	Dimensionless
T	Temperature	K
∇T	Temperature gradient	K m^{-1}
t	Time	s
u	Specific internal energy	J kg^{-1}
V	Volume	m^3
V_p	P-wave velocity	m s^{-1}
\dot{V}, \hat{V}	Darcy flux; vector, magnitude	$\text{m}^3 \text{m}^{-2} \text{s}^{-1}$
v	Fluid velocity	m s^{-1}
x, x'	Coordinates; vector, magnitude	m
	Cross-sectional area	m^2
α	Thermal diffusivity	$\text{m}^2 \text{s}^{-1}$
$\varepsilon_{ij}^e; \varepsilon_{ij}^p$	Elastic; plastic strain tensor	Dimensionless
κ_{fluid}	Diffusivity of fluid	$\text{m}^2 \text{s}^{-1}$
μ	Fluid viscosity	Pa s
μ^K	Chemical potential of the K^{th} chemical component	J kg^{-1}
∇^K	Gradient in the chemical potential of the K^{th} chemical component	$\text{J kg}^{-1} \text{m}^{-1}$
τ	Residence time	s
ξ	Extent of a mineral reaction	$0 \leq \xi \leq 1$; dimensionless
$\dot{\xi}$	Rate of a mineral reaction	s^{-1} or mol s^{-1}
ν	Stoichiometric coefficient	Dimensionless
ρ	Density	kg m^{-3}
ρ_{fluid}	Fluid density	kg m^{-3}
ω	Vorticity	Dimensionless
ω_k	Characteristic rate of decay	s^{-1}
σ	Surface tension	Pa
σ_{tensile}	Tensile; compressive strength of rock	Pa
$\sigma_{\text{compressive}}$	Surface heat transfer coefficient	$\text{W m}^{-2} \text{K}^{-1}$
ϕ	Instantaneous porosity	Dimensionless
φ	Concentration field	Dimensionless
λ	Lyapunov exponent	Dimensionless
λ	Control parameter	Dimensionless
λ_k	An intensive variable	Depends on the variable
Λ	Local finite-time Lyapunov exponent measuring the stretching history	Dimensionless
Φ	Dissipation functional	$\text{J kg}^{-1} \text{s}^{-1}$
Ψ	Specific Helmholtz energy	J kg^{-1}
∇	Gradient operator	

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