Mineral Systems as Chemical Reactors with no Mathematics

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Mineral Dynamics
Fremantle

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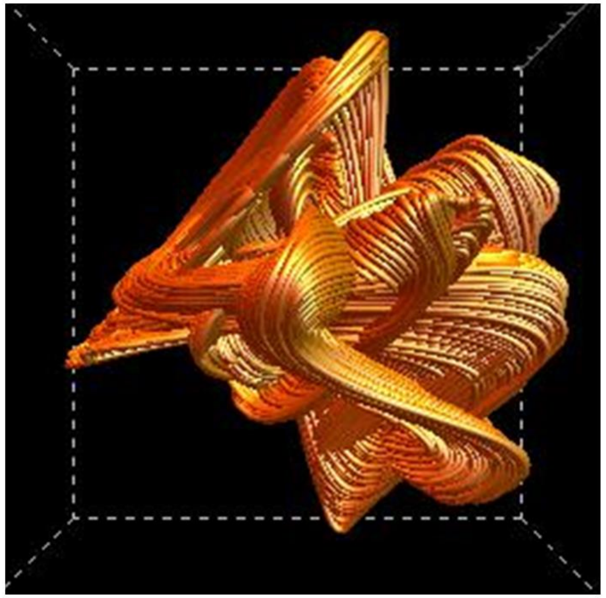
Session 3. 09.45 – 10.30



What is a mineral system? What is not a mineral system?

Coupled nonlinear processes

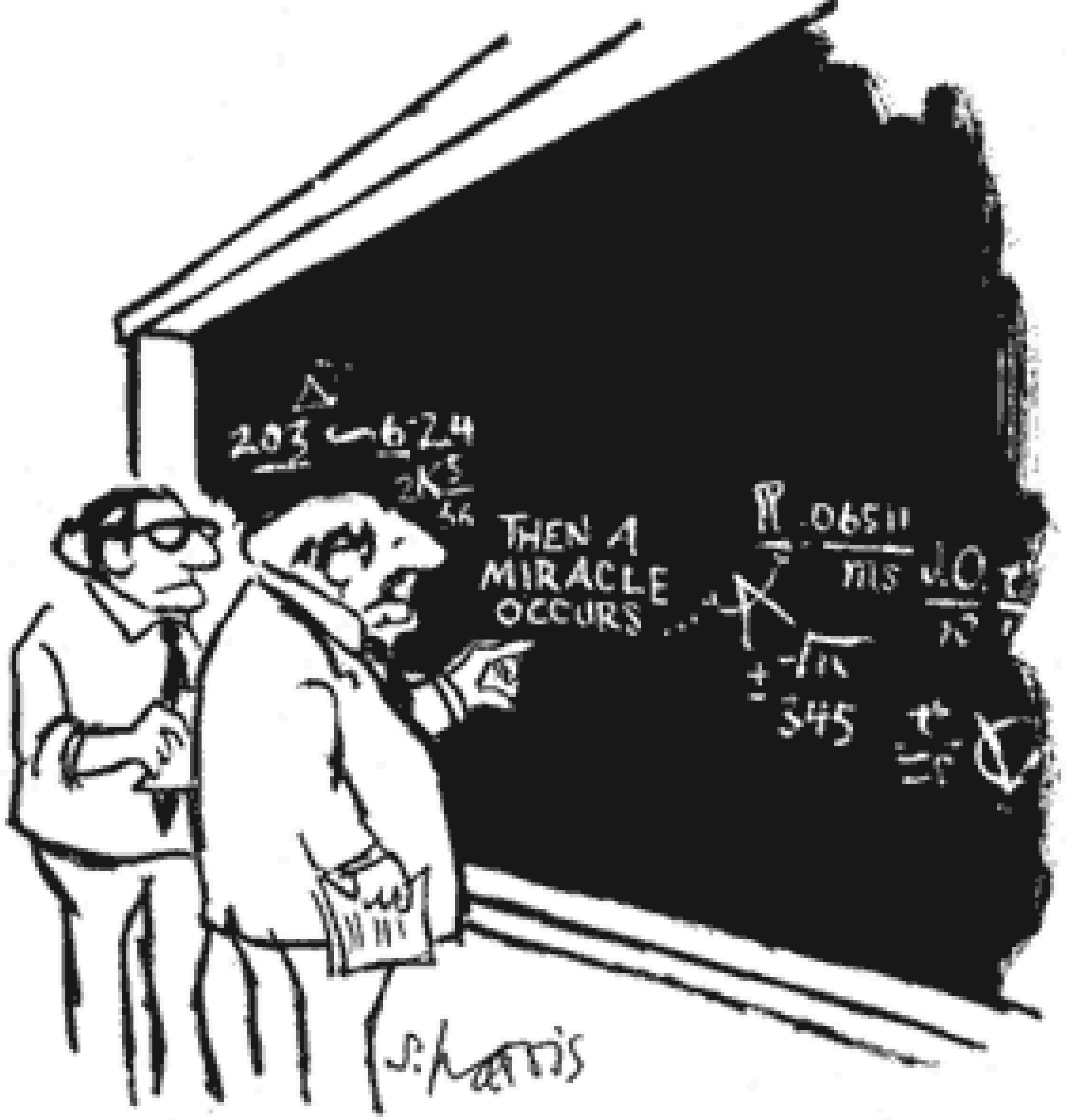
Takens' theorem and attractors

Some examples

Feinman, 1964.

***You cannot prove a vague theory wrong*.**

The Feinman Lectures. Addison. http://www.feinmanlectures.caltech.edu.



"I THINK YOU SHOULD BE MORE EXPLICIT HERE IN STEP TWO."

What is a mineral system? What is not a mineral system?

- **A mineral system is any region in the Earth's lithosphere where mineralising processes operate.**

- **A mineral system is defined by**
  1. **The boundaries**
  2. **The processes that operate within the boundaries**
  3. **The processes that operate outside the boundaries and that contribute mass and energy to the system**
  4. **The competitive processes that define the growth of the system.**

- **A permissible mineral system must**
  1. **Obey the first and second laws of thermodynamics.**

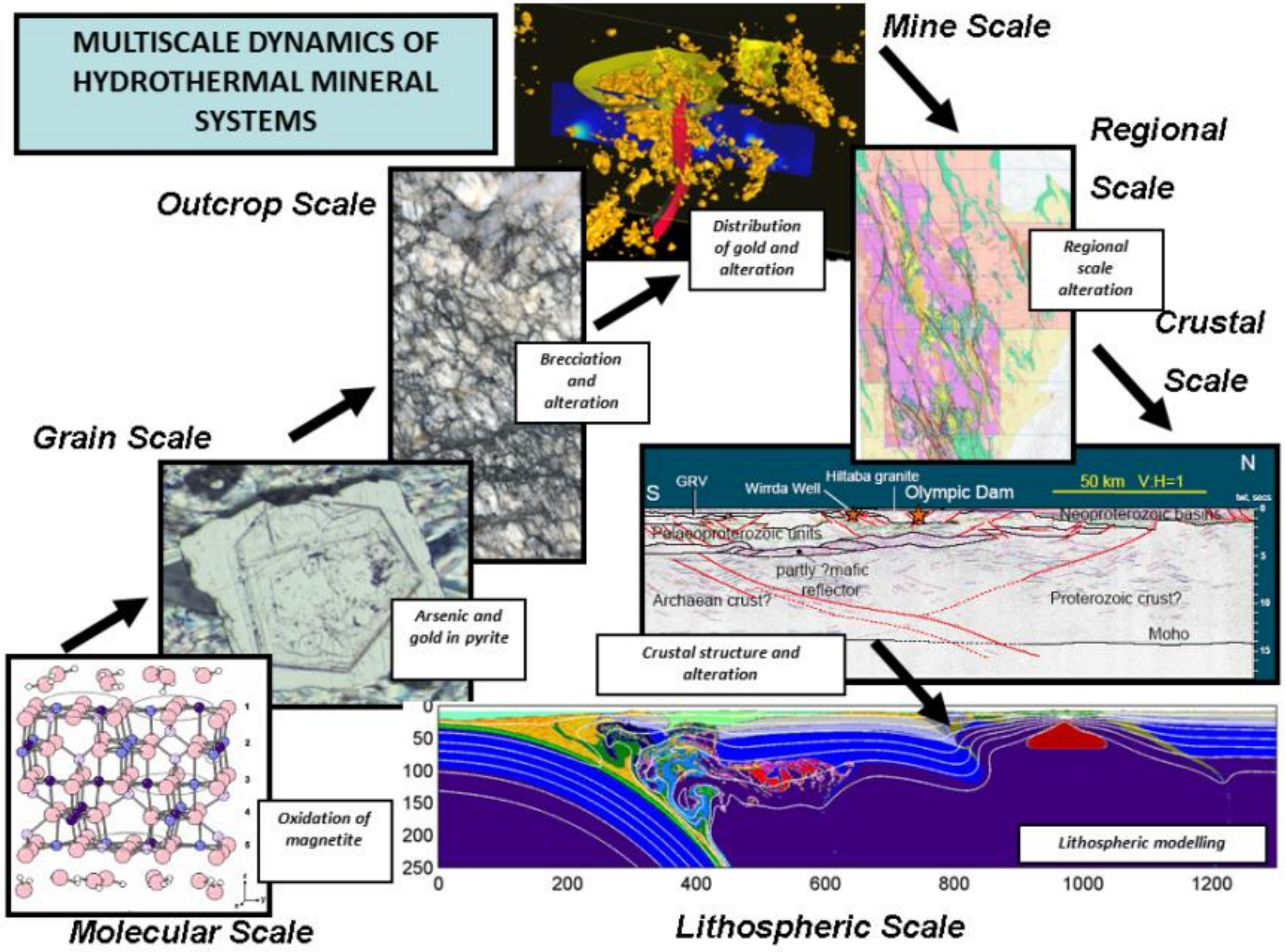
     Energy and mass are conserved

     Net entropy production is equal to or greater than zero.

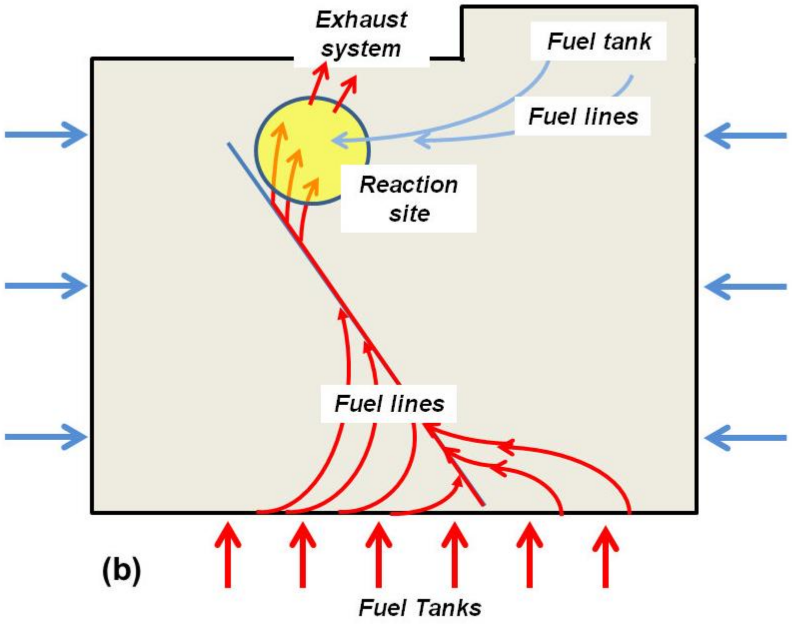
     Stationary states correspond to zero net entropy production.

     Equilibrium corresponds to no dissipative processes operating.
  2. **Obey the principles of mechanics.**

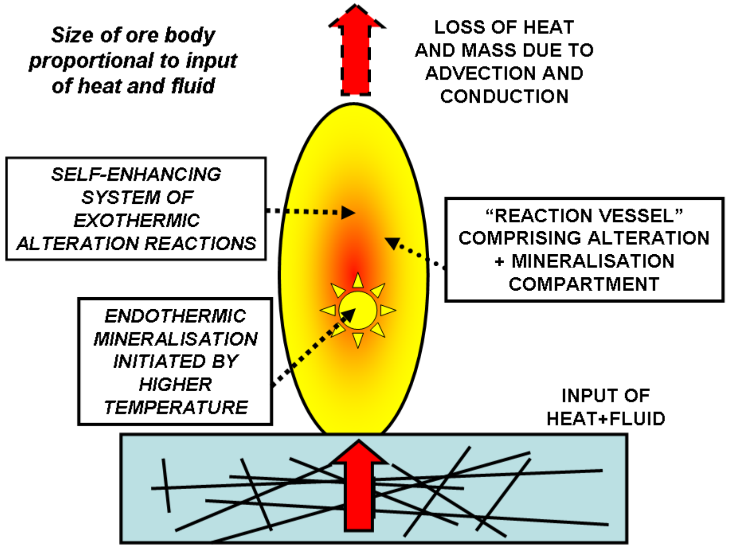
     Continuity and The balance laws.



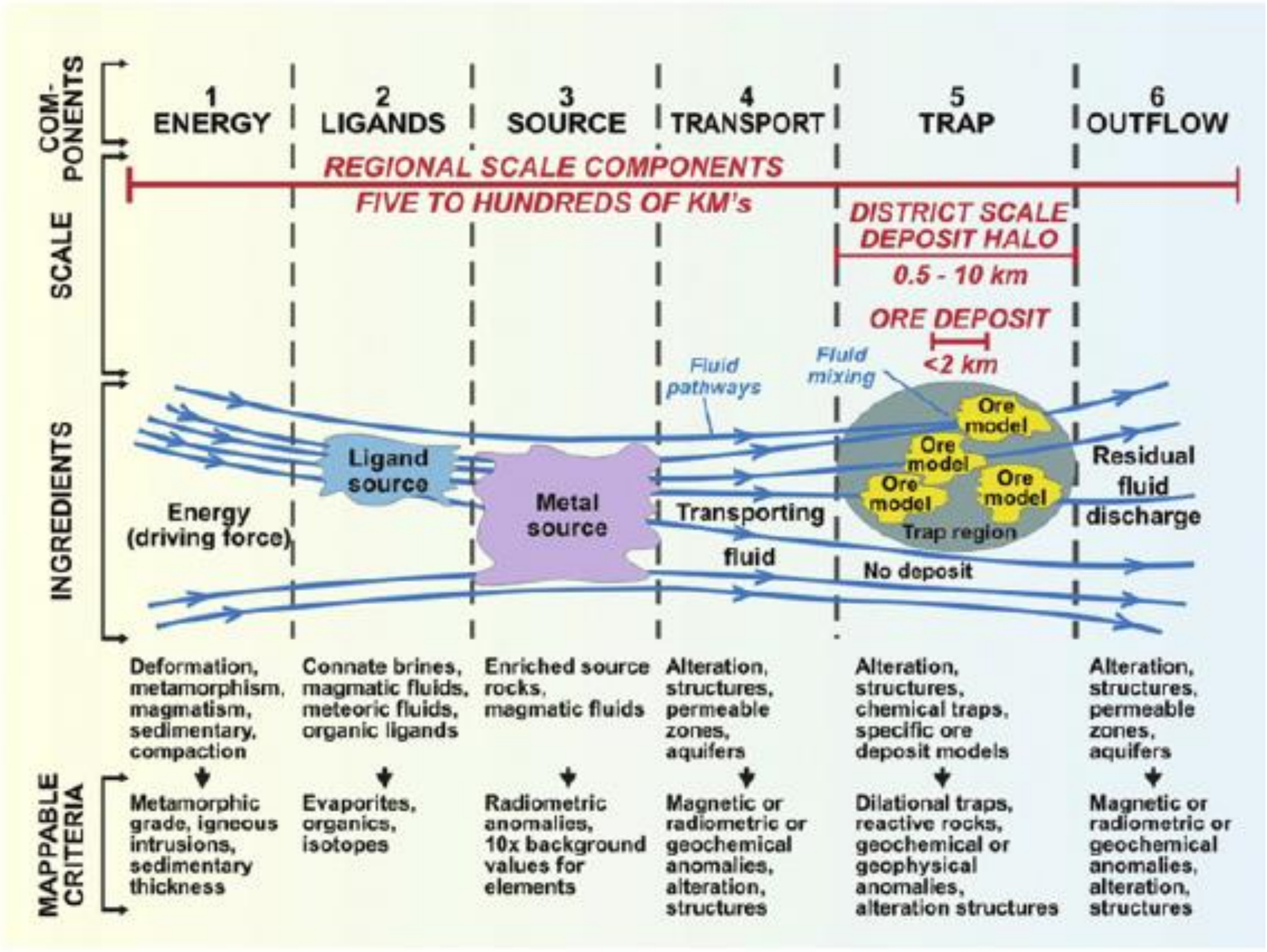
MULTISCALE DYNAMICS OF HYDROTHERMAL MINERAL SYSTEMS
Mine Scale
Regional Scale
Outcrop Scale
Distribution of gold and alteration
Regional scale alteration
Crustal Scale
Brecciation and alteration
Grain Scale
N
S
GRV
Wirrda Well
Hiltaba granite
Olympic Dam
50 km V:H=1
Neoproterozoic basins
Palaeoproterozoic units
partly ?mafic reflector
Archaean crust?
Proterozoic crust?
Moho
Arsenic and gold in pyrite
Crustal structure and alteration
Oxidation of magnetite
Lithospheric modelling
0
50
100
150
200
250
0
200
400
600
800
1000
1200
Molecular Scale
Lithospheric Scale



Exhaust system
Fuel tank
Fuel lines
Reaction site
Fuel lines
(b)
Fuel Tanks



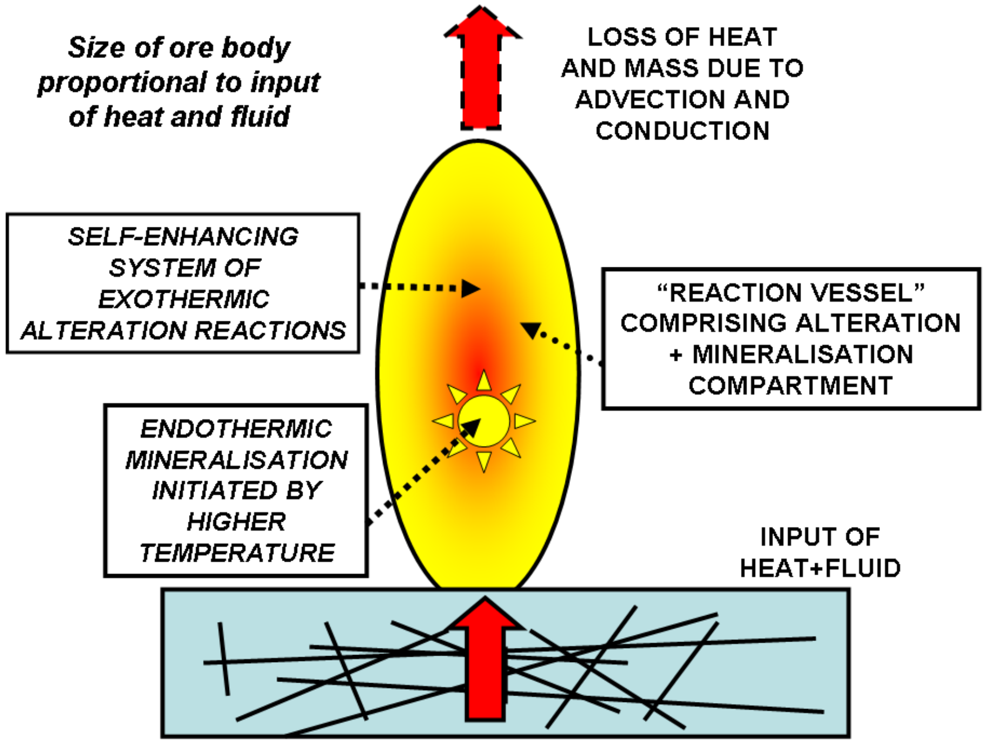
Size of ore body proportional to input of heat and fluid
LOSS OF HEAT AND MASS DUE TO ADVECTION AND CONDUCTION
SELF-ENHANCING SYSTEM OF EXOTHERMIC ALTERATION REACTIONS
"REACTION VESSEL" COMPRISING ALTERATION + MINERALISATION COMPARTMENT
ENDOTHERMIC MINERALISATION INITIATED BY HIGHER TEMPERATURE
INPUT OF HEAT+FLUID



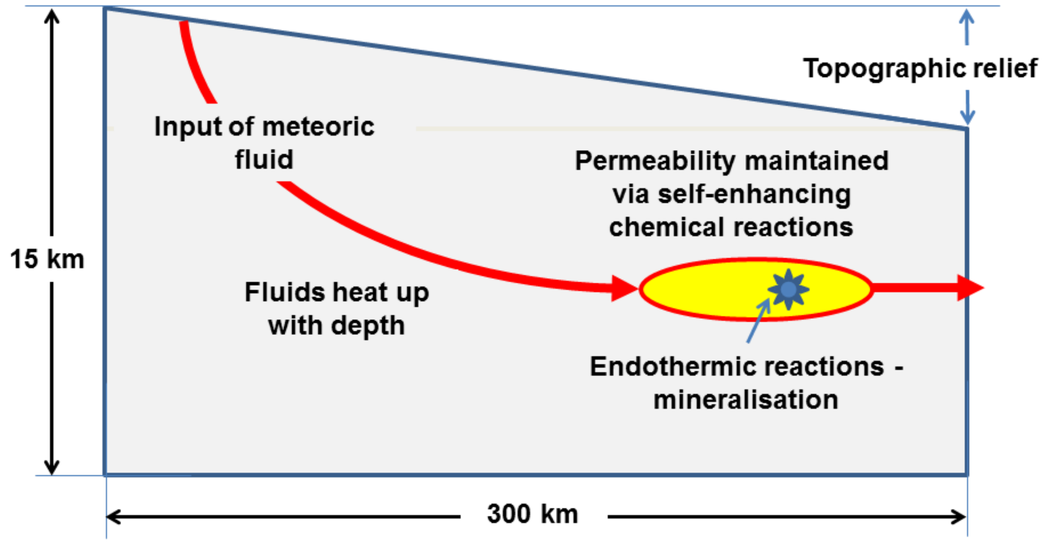
Most published "mineral systems" are not systems; they are cartoons.

Many do not obey the laws of thermodynamics and few obey the laws of mechanics

Two end member mineral systems

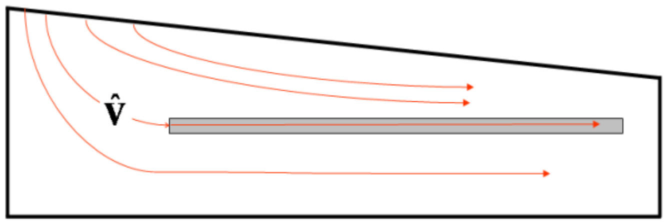


One of the end member type of hydrothermal system:
A flow controlled mineralising system.
Orogenic gold
Porphyry copper
IOCG

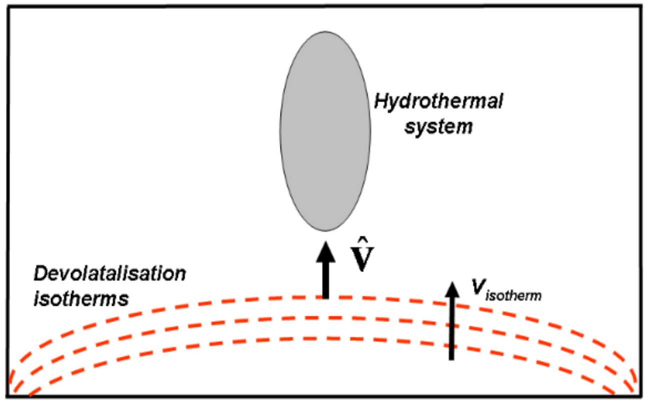


A second end member type of hydrothermal system.
A hydraulic head controlled system.
MVT sedimentary Pb-Zn
Some aspects of porphyry copper and of epithermal gold

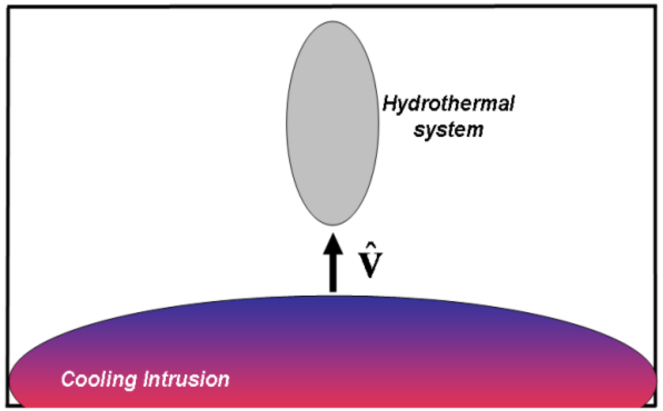
EXAMPLES OF OPEN FLOW SYSTEMS



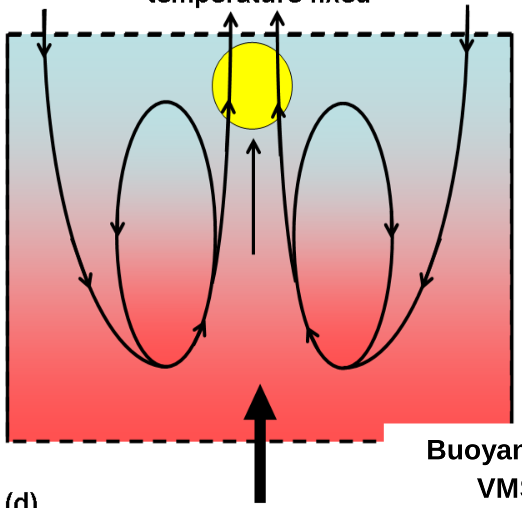
(a) **Hydraulic potential controlled: MVT-deposits**



(b) **Flow controlled: orogenic gold, IOCG-deposits**



(c) **Flow controlled: Porphyry, orogenic gold, IOCG-deposits**



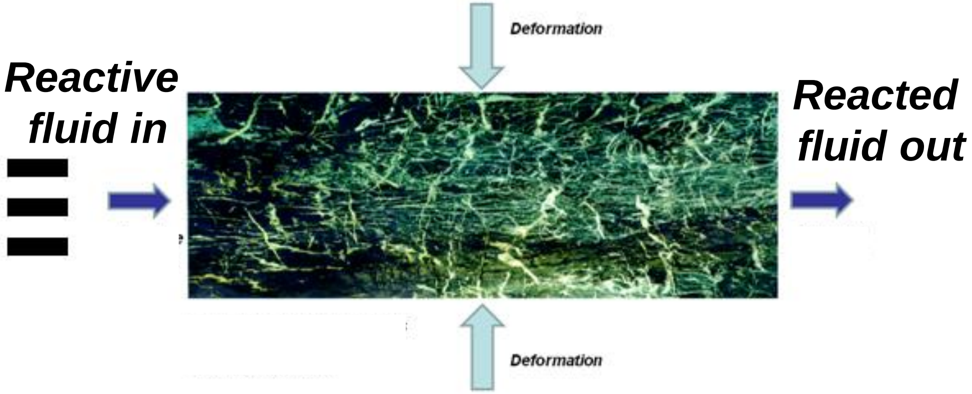
(d) **Buoyancy controlled: VMS-deposits**

An important difference between a true systems approach to mineralising processes and the classical “static” approach is the way in which mineral reactions are treated.

=

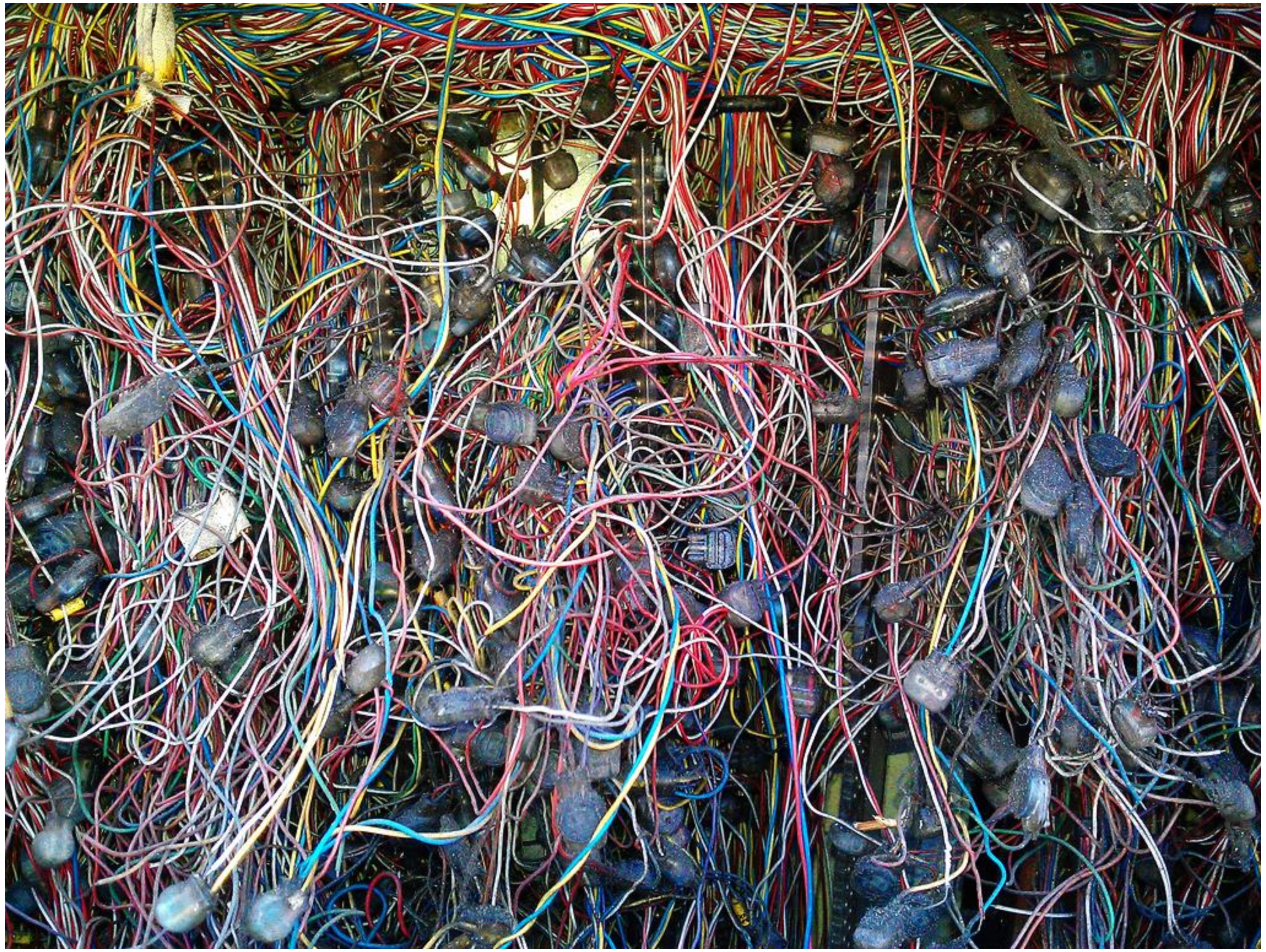
In the classical approach mineral reactions represent a reacting system as a closed beaker of fluid at chemical equilibrium with no consideration of the influence of mass and heat flow/generation on the mineralising processes.

In a systems approach all processes are coupled, the system is open and is driven far from equilibrium by fluxes of heat and mass



Heat and mass generated internally

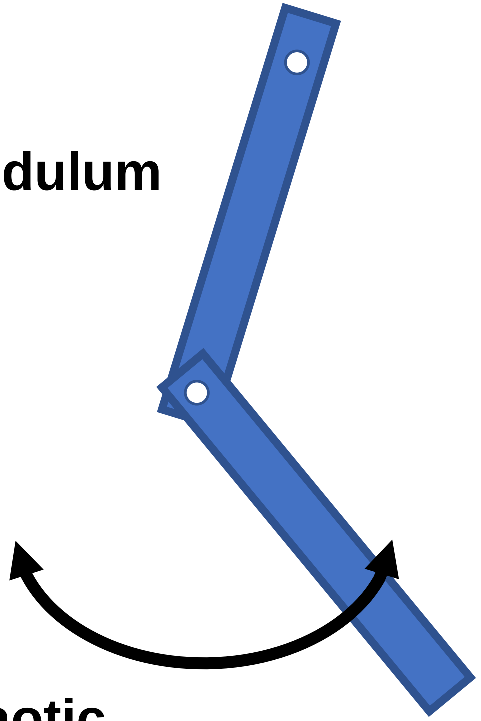
Critical thinking is nice to have



Complicated but not chaotic.

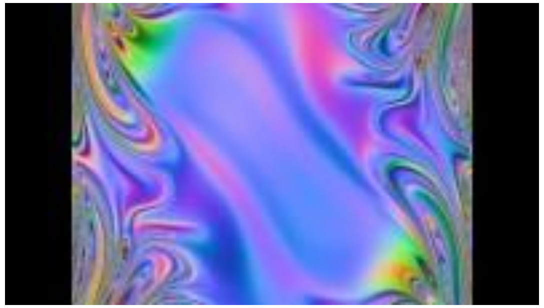
Behaviour can be understood by mapping all the components.

Double pendulum

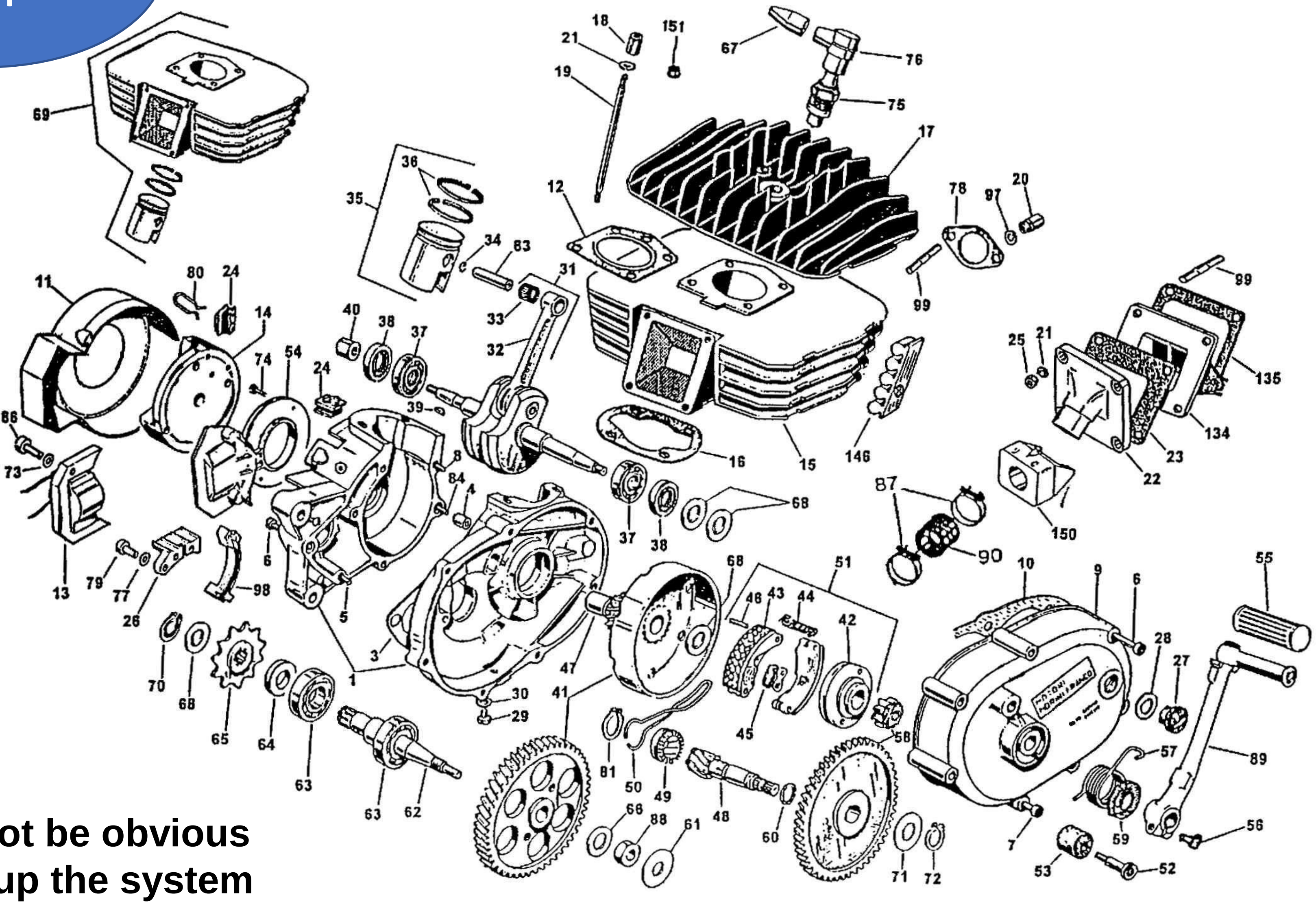


Simple but chaotic.

Behaviour can not be understood by mapping all the components.

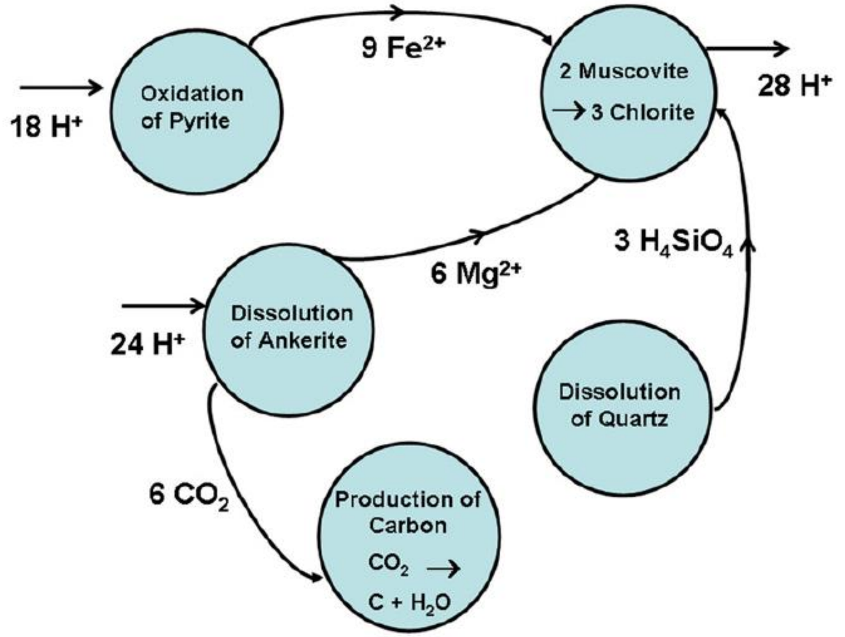


Where is the bit called speed?



The behaviour of a system may not be obvious from the components that make up the system

Coupling of reaction processes



Most alteration reactions are exothermic and have negative ΔV

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

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

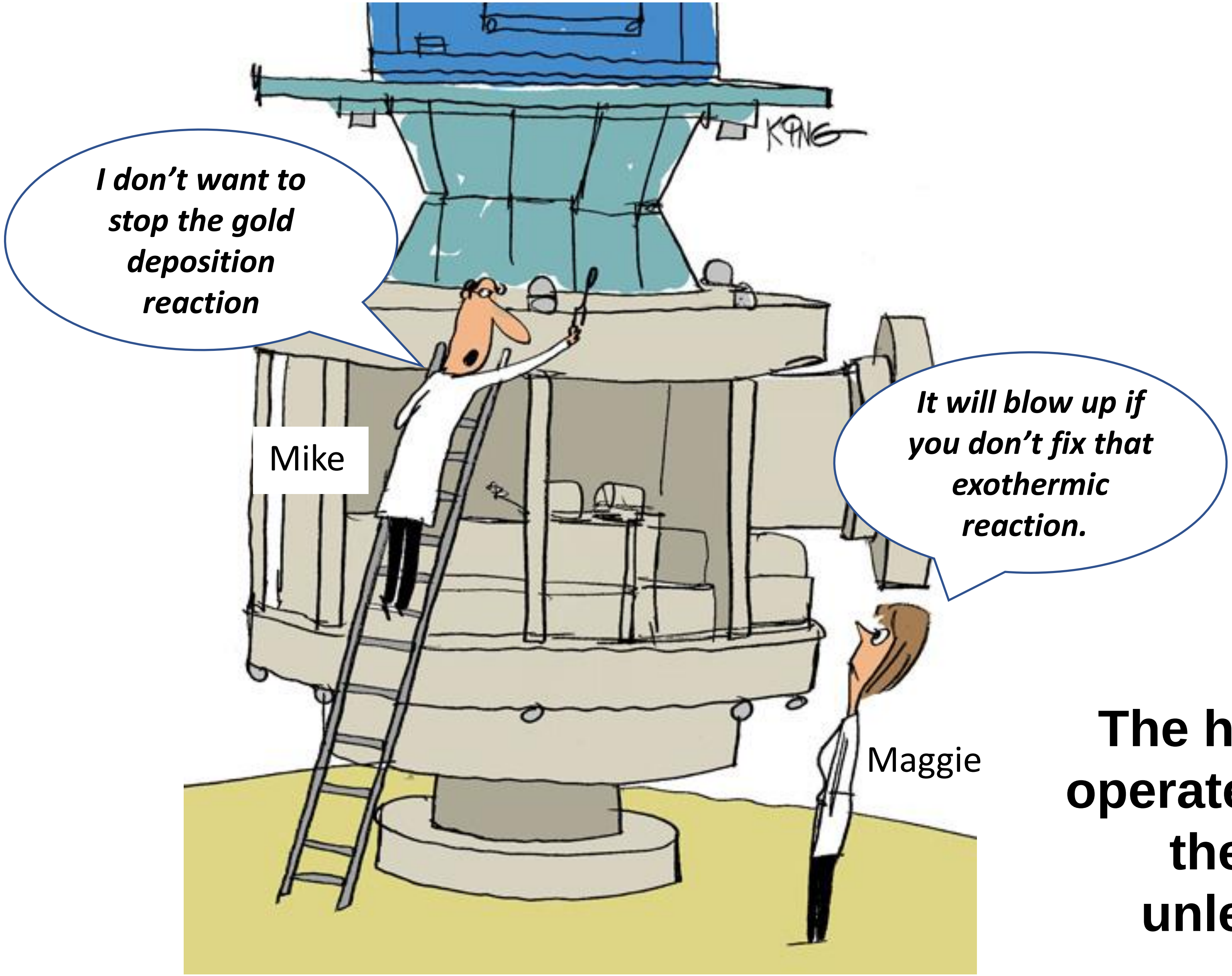
ΔH_R and $\Delta V_R/V_{RCT}$ are based on the compilation by Berman (1988, programme update 1992) and refer to standard state conditions 298 K, 100 kPa. ΔH_R/mole H_2O is given for water (liquid). $\Delta V_R/V_{RCT}$ is calculated with respect to the liquid volume of H_2O. ΔV_R – volume of reaction,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

Most alteration reactions are equal volume replacement

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

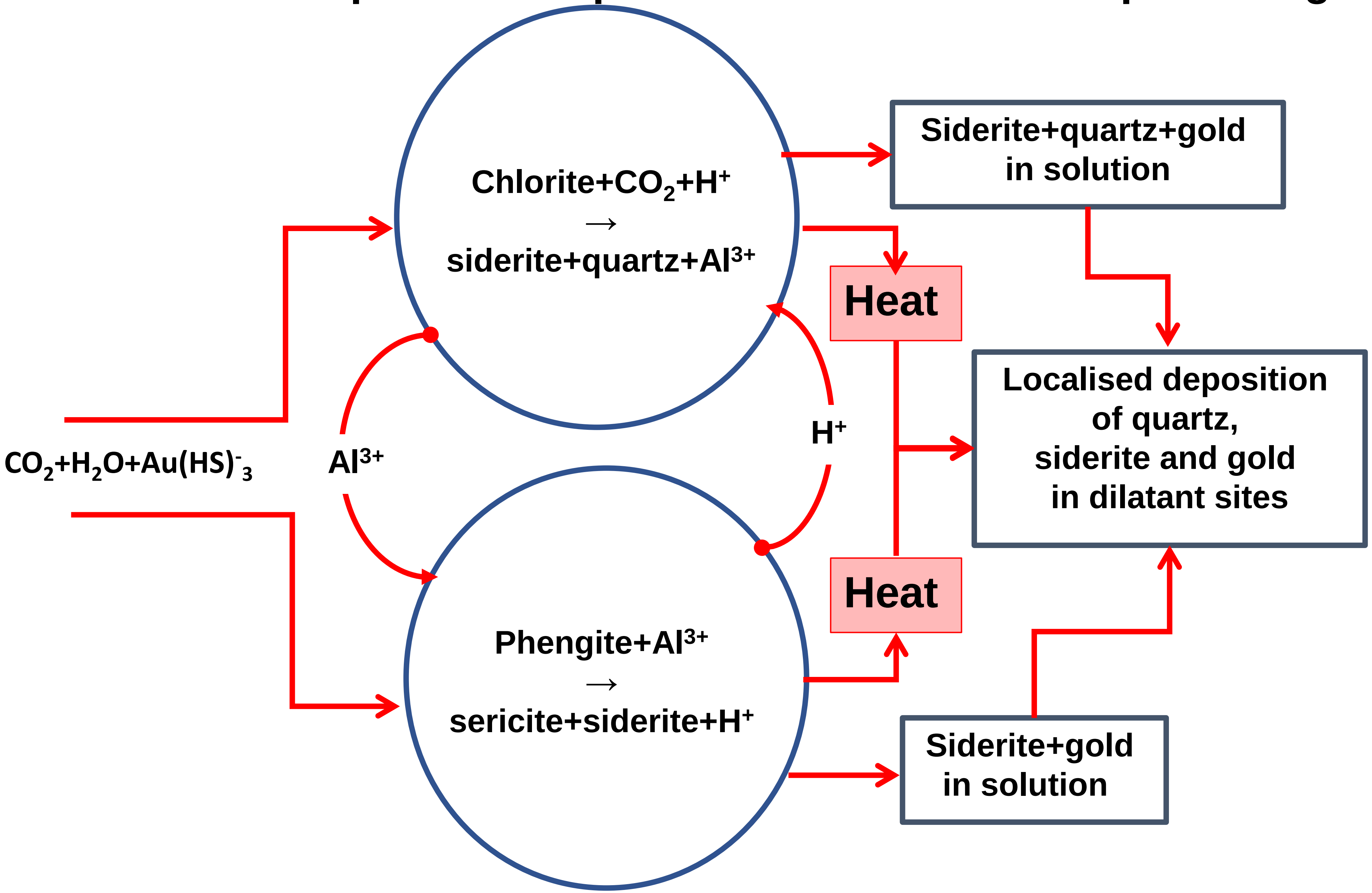
This reaction converts 77 moles of $\left(SO_4^{2-}\right)$ to 86 moles of $\left(SO_4^{2-}\right)$

and incidentally, also converts 42 moles of Fe^{3+} to 50 moles of Fe^{2+}.



The hydrothermal reactor cannot operate efficiently- that is - produce the maximum possible gold unless all parts of the system Interact optimally.

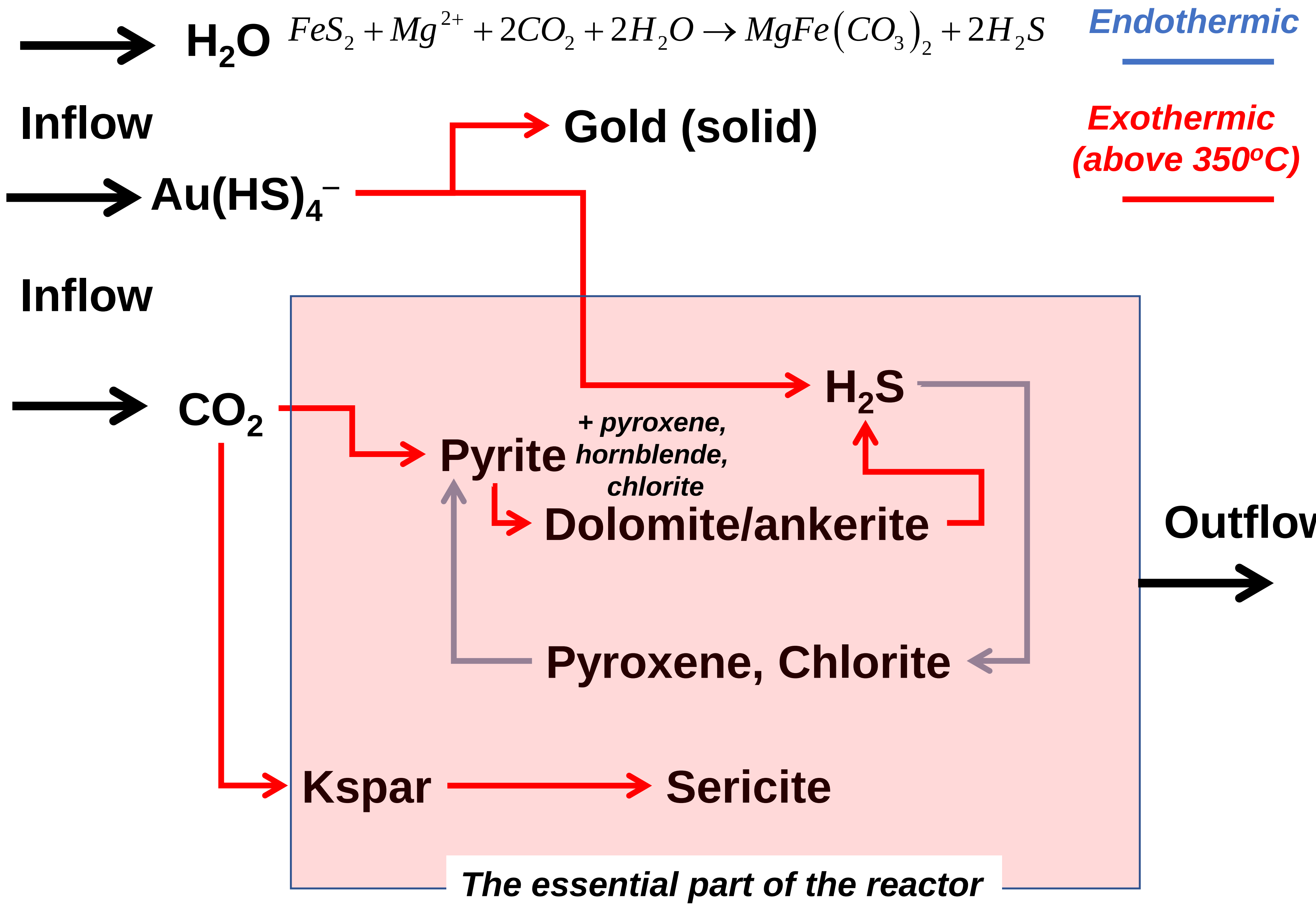
An example of a coupled set of reactions that produce gold



Another example

$$2H_2S + Fe^{2+} \rightarrow FeS_2 + 4H^+$$

$$FeS_2 + Mg^{2+} + 2CO_2 + 2H_2O \rightarrow MgFe(CO_3)_2 + 2H_2S$$



As a summary:

1. Mineralising systems are giant open flow chemical reactors driven far from equilibrium by the influx of mass and heat.

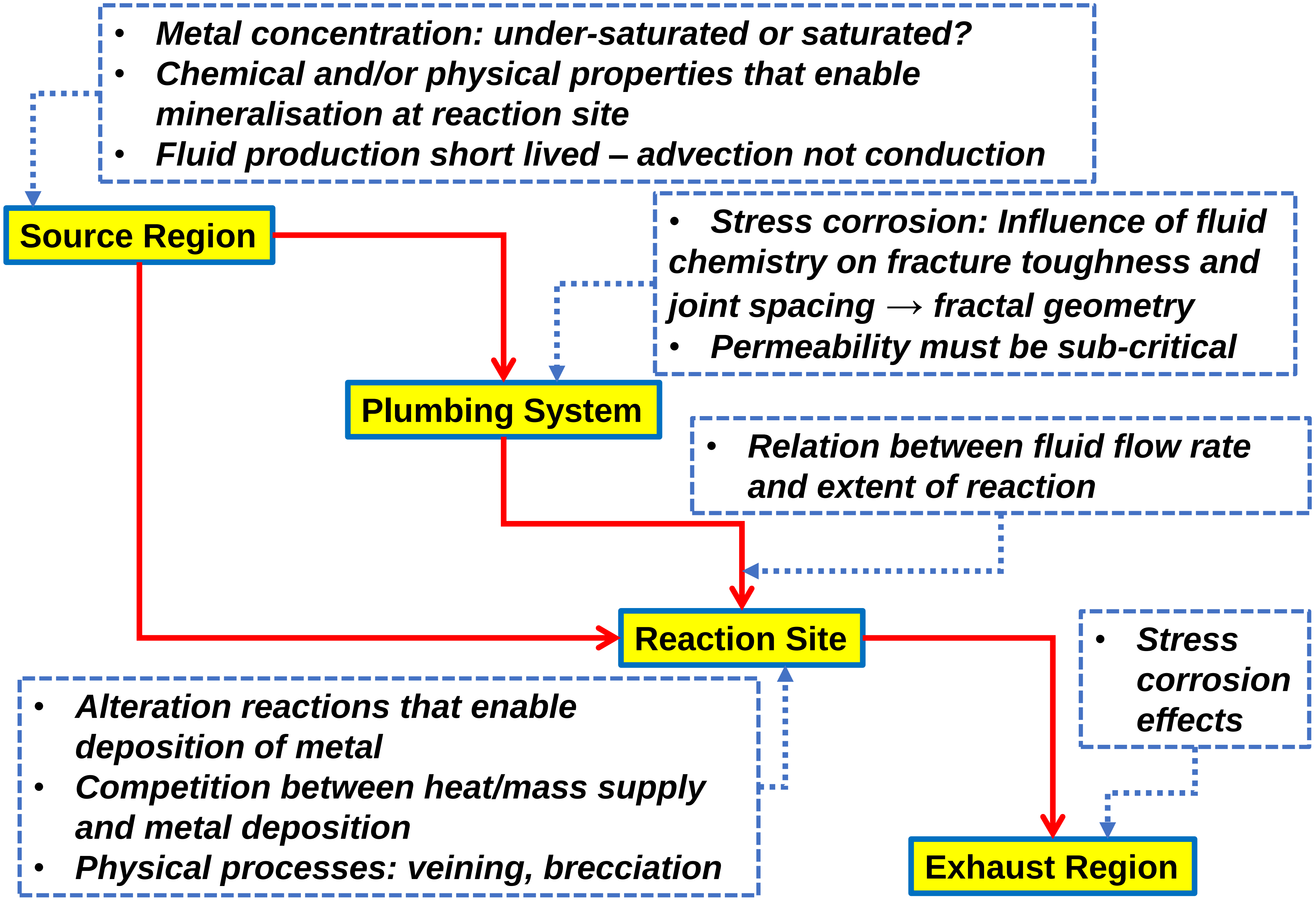
2. The alteration systems and deformation are exothermic and supply heat but need fluids.

3. Deposition of sulfides, gold, quartz and carbonates are endothermic and need heat.

4. All the processes are coupled and the coupling needs to be optimal to produce a superior ore system.

5. The chemical and physical nature of many reactions means they are both autothermal and autocatalytic resulting in nonlinear oscillatory and irregular behaviour.

THE MINERALISING SYSTEM



The ultimate outcome of the competition between exothermic and endothermic processes, the autocatalytic and autothermal behaviours, the large ΔV's of reactions and the production and consumption of fluids is nonlinear behaviour where irregularity is the norm and prediction seems impossible.

However, since the system obeys the laws of physics and chemistry, the system behaviour is deterministic and not random.

We need a foundation for examining such systems and this is given by Takens' theorem.

Takens' Theorem (1981):

In any coupled dynamical system the behaviour of one component (say arsenic or sericite) reflects the behaviour of all other coupled components.

This means that just one component can be used to predict the behaviour of all other coupled components.

This is because the behaviour of every single component depends on the behaviour of all others.

Takens' Theorem 1981): simple but profound.

The behaviour of all components in a system is restricted to lie on an *attractor* for that system.

An attractor describes all the possible states that the system can evolve through.

An attractor exists in N-space where N is the number of independent processes operating.

An attractor can be drawn using any one component using a displacement process which we explore below.

Takens' Theorem 1981): simple but profound.

Dynamical systems are characterised by three features:

1. **Multifractal behaviour in space and time. A multifractal is a set of fractals embedded in each other.**

2. **Recurrence. The system repeats itself in a statistical sense in space and time.**

3. **The probability distribution of a component reflects the growth of the system.**

Let us now look at the behaviour of some simple nonlinear systems using XCEL to see the development of deterministic chaos and the application of Takens' theorem

A1 = 0.1

B1 = 2*A1

A2 = B1

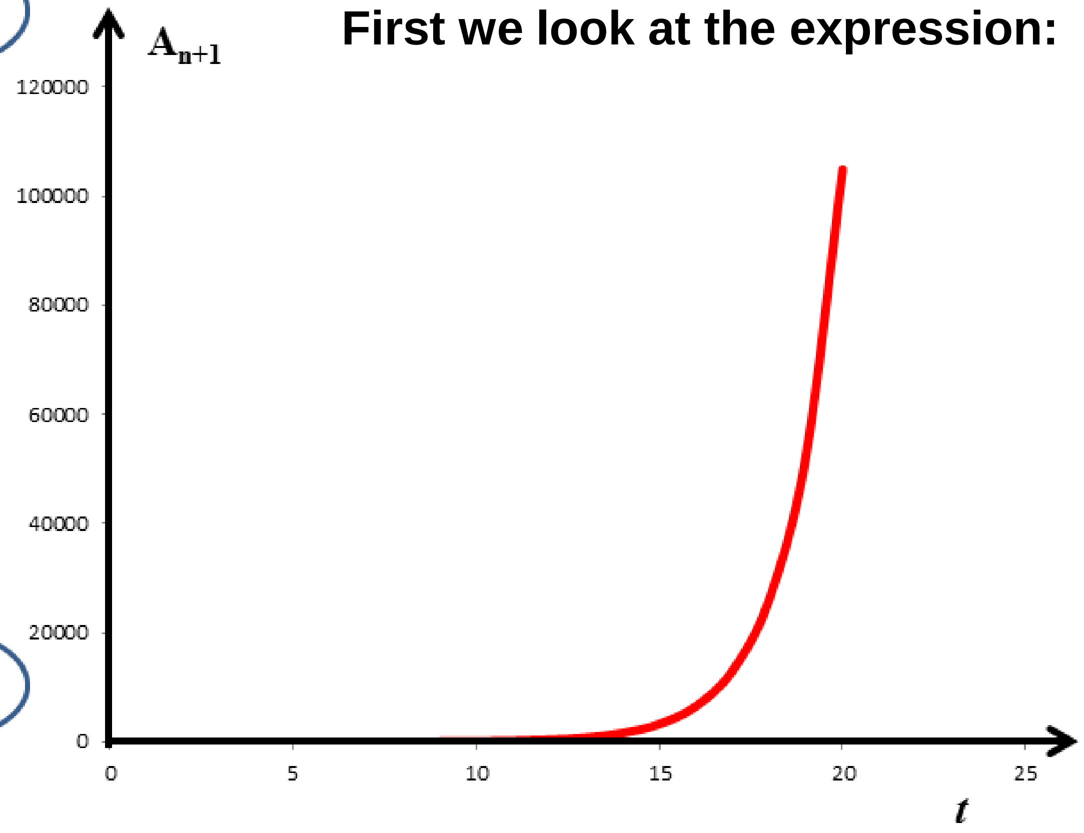
Column A

Column B

A_n	A_{n+1}
0.1	0.2
0.2	0.4
0.4	0.8
0.8	1.6
1.6	3.2
3.2	6.4
6.4	12.8
12.8	25.6
25.6	51.2
51.2	102.4
102.4	204.8
204.8	409.6
409.6	819.2
819.2	1638.4
1638.4	3276.8
3276.8	6553.6
6553.6	13107.2
13107.2	26214.4
26214.4	52428.8
52428.8	104857.6

(a)

First we look at the expression: $x_{n+1} = \alpha x_n$



(b)

Now we introduce some complexity in the form of competition: $x_{n+1} = \alpha x_n (1 - x_n)$

A1 = 0.1

A2 = B1

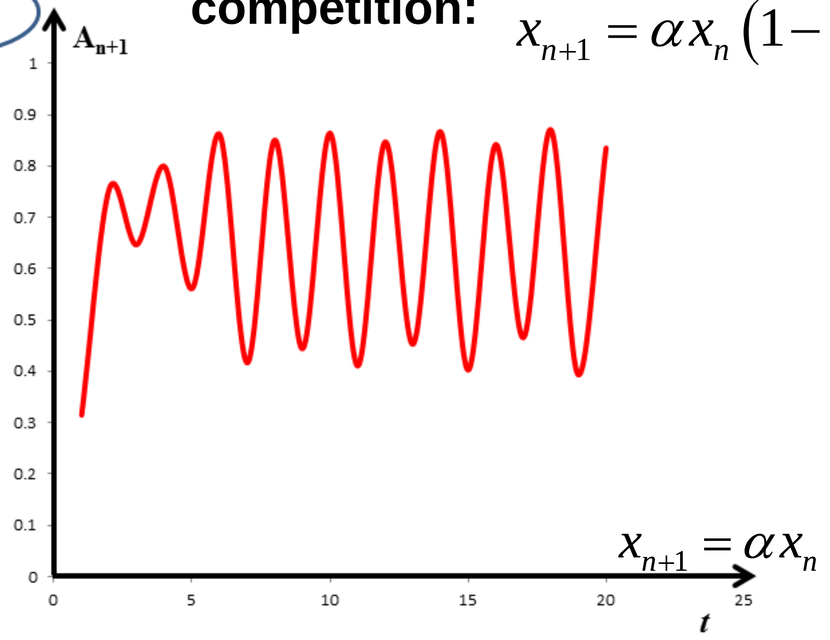
B1 = 3*A1*(1-A1)

Column A

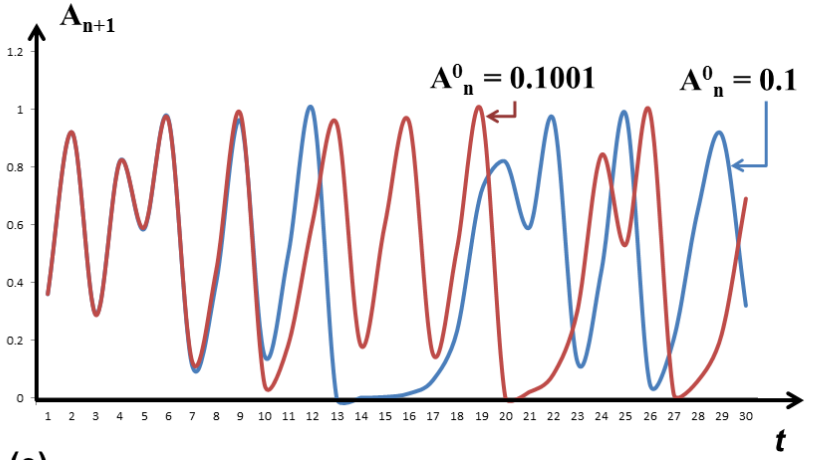
Column B

A_n	A_{n+1}
0.1	0.315
0.315	0.755213
0.755213	0.647033
0.647033	0.799335
0.799335	0.561396
0.561396	0.861807
0.861807	0.416835
0.416835	0.850793
0.850793	0.444306
0.444306	0.864144
0.864144	0.410898
0.410898	0.847213
0.847213	0.453051
0.453051	0.867285
0.867285	0.402856
0.402856	0.84197
0.84197	0.465697
0.465697	0.870882
0.870882	0.393564
0.393564	0.83535

(c)

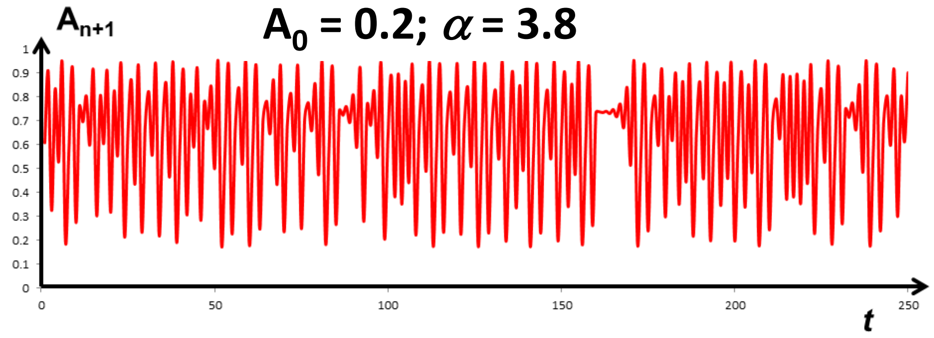


(d)

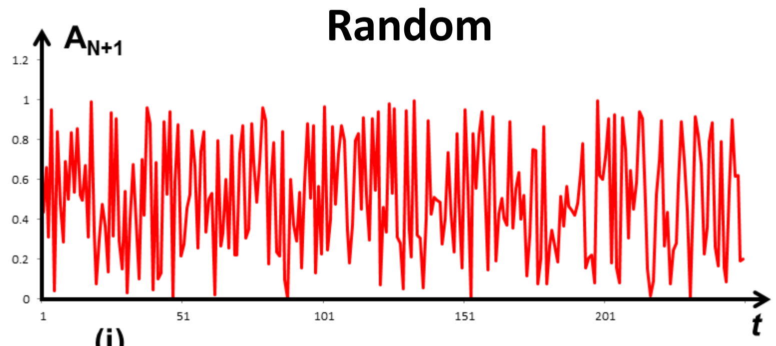


(e)

Sensitivity to initial conditions

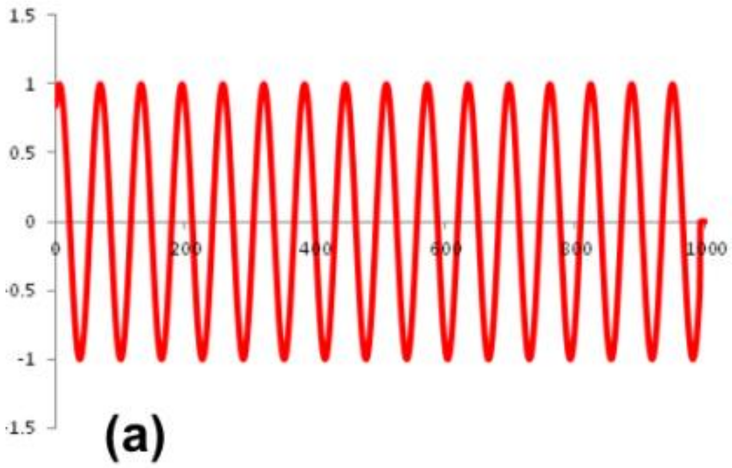


(f)

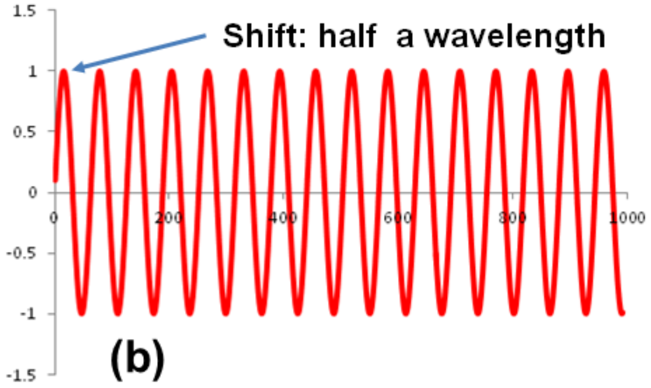


(i)

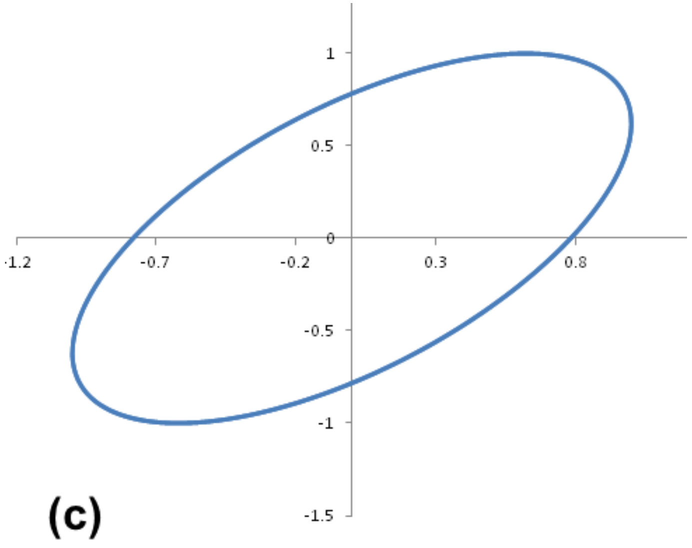
Now we look at Takens' theorem and the construction of attractors



A sine wave



A sine wave shifted a little to the right



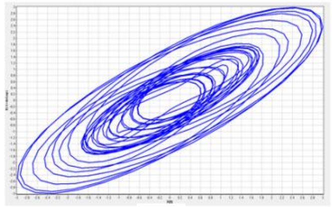
The attractor for a sine wave. If we know one point on the attractor, we can predict all other points

Some other attractors

Quasiperiodic

$$y=\sin x+\sin\left(\sqrt{2}x\right)+\sin\left(\sqrt{5}x\right)+\sin\left(\sqrt{15}x\right)$$

(a)



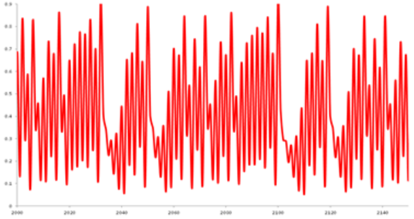
(b)

(c)

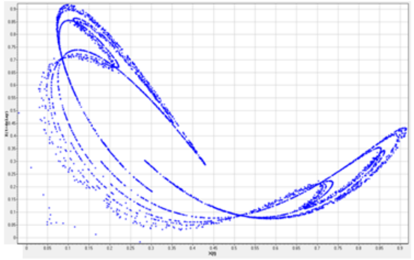
Generalised Hénon (Sprott, 2003, p130)

$$x_{n+1}=-0.4x_n+1.7y_n+1.1x_n^2-3.3x_ny_n$$

$$y_{n+1}=x_n$$



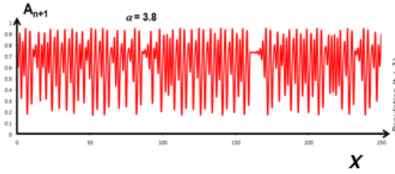
(d)



(e)

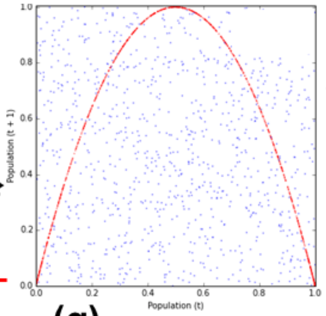
Logistic

$$x_{n+1}=\alpha x_n\left(1-x_n\right)$$

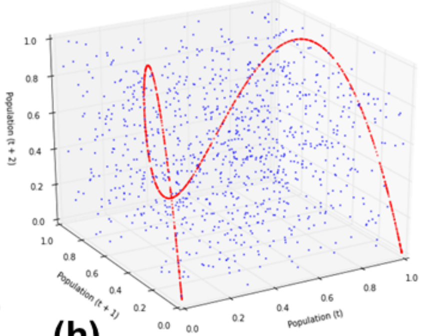


(f)

Random •
Logistic

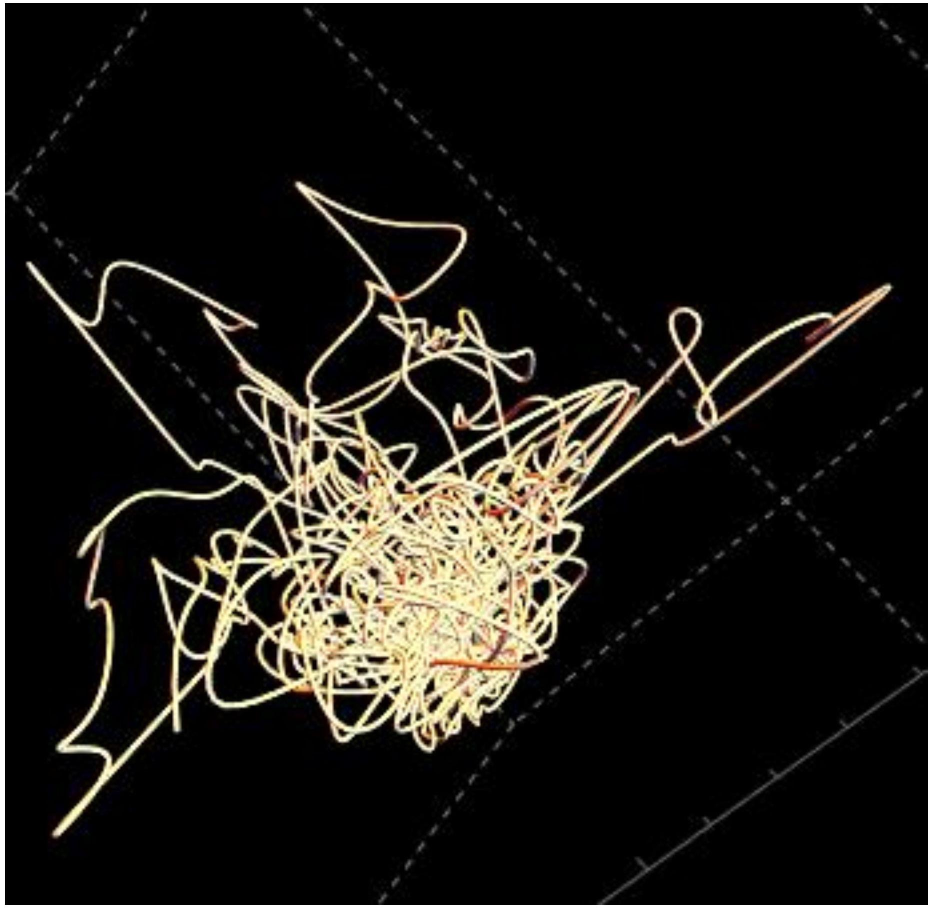


(g)



(h)

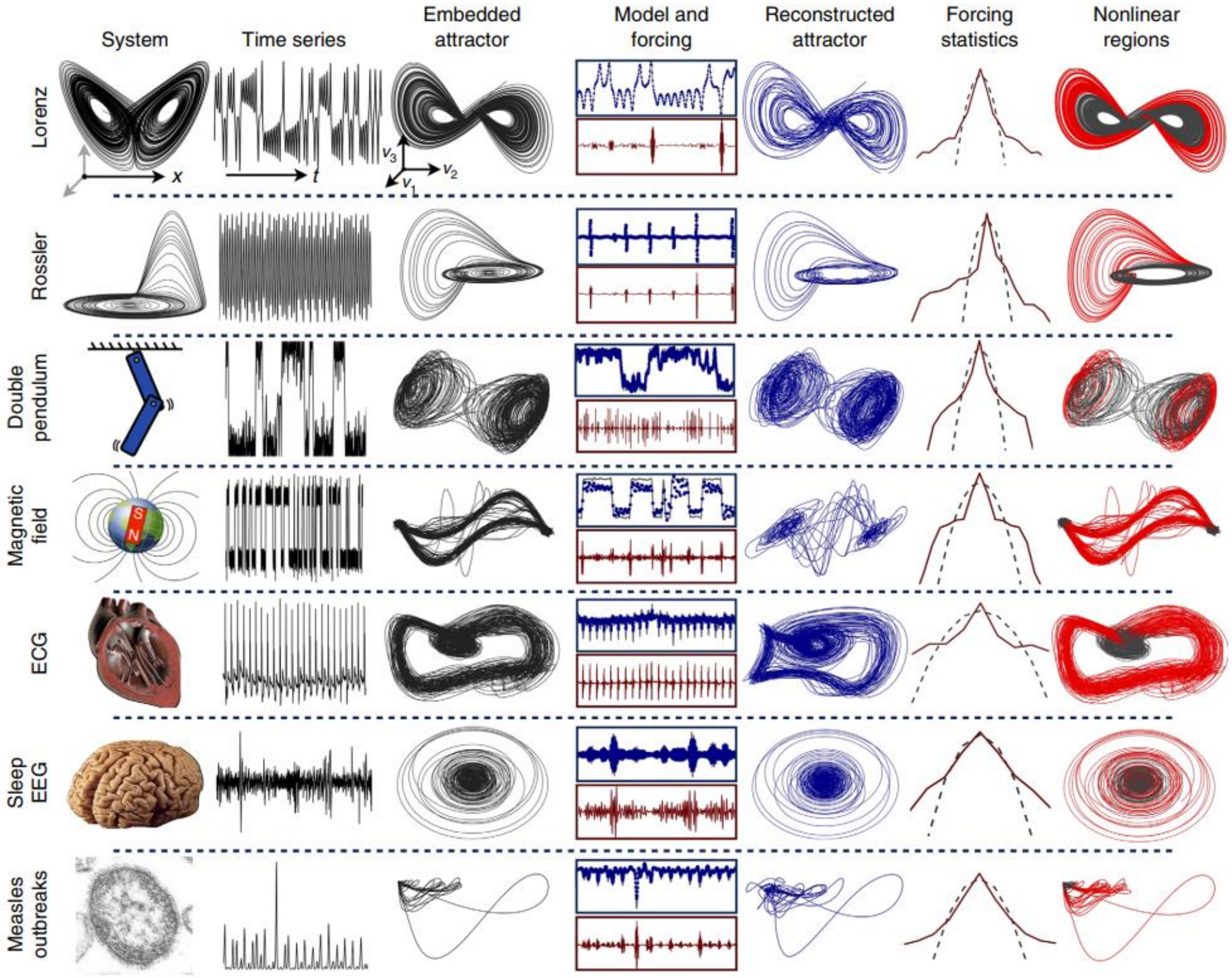
Attractor in 3D for gold Sunrise Dam.



This is the projection of a seven dimensional attractor into 3 dimensions

NATURE COMMUNICATIONS | DOI: 10.1038/s41467-017-00030-8

Brunton et al. Chaos as an intermittently forced linear system



Some other examples

An anatomy of a mineralising system.

Mineralising systems are nonlinear dynamical systems.

Nonlinear systems behave chaotically but are highly organised and exhibit coherent structures and patterns.

The problem is to delineate and quantify these patterns.

The ultimate aim is to predict behaviour and patterns.

Characteristics of a mineralising system.

- **Operate far from equilibrium driven by the fluxes of energy and mass.**
- **Signals from drill core are a one dimensional projection of complex interactions between mineral reactions, deformation, heat flow and mass flow.**
- **Some interactions are strong and tend to control everything that happens.**
- **Some interactions are weak and are slaved to the strong interactions.**
- **In order to understand te mineralising process we need to understand which are the strong and weak interactions**

The analysis of any nonlinear dynamical system depends on Taken' s embedding theorem which states that

The full dynamics of a dynamical system may be uncovered from the data series of a single point measurement.

This allows the construction of an attractor for the system that is topologically equivalent to the the real attractor for the system.

These tasks are relatively straight forward for low dimensional systems where few processes operate. For high dimensional systems with many physical and chemical processes operating the task can be quite daunting.

The issues we need to address.

1. How many processes are operating?
2. Which are the strong ones and which are the weak ones?
3. Are there any long range correlations?
4. What spatial scales are involved?
5. What are the correlations between minerals in the system?
6. Are nonlinear predictions possible?
7. Can the alteration assemblage minerals be used to predict mineralisation?
8. Which ones are best?
9. What are the probability distributions for mineralisation and for alteration minerals?
10. Do these distributions change within the ore system? Do such changes correlate with grade?