

# Quantitative Characterization of Hydrothermal Systems and Reconstruction of Fluid Fluxes: the Significance of Advection, Disequilibrium, and Dispersion

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**Abstract.** Fossil hydrothermal systems are increasingly interpreted using the transport theory, which allows us to convert the extent of alteration and precipitation changes into an estimate of net (time-integrated) fluid flux. Since the compositional gradients and consequent reactions are produced by a combination of several independent factors, potentially acting to similar extent, we propose various ways to continuously bridge situations and introduce mass transport descriptors, which would facilitate quantitative description of conventional geological observations. Hydrothermal systems are divided, based on the Péclet number, into advection-dominated, which mainly include hydrothermal veins, fracture- and shear zone-controlled fluid flow, and diffusion/dispersion-dominated, mainly forming at high temperatures and during metamorphic devolatilization. Time scales of hydrothermal events dictate the length scale of advective vs. diffusive transport and extent of alteration reactions, related by the Damköhler number. Rapid hydrothermal events are dominated by advective transport, which promotes disequilibrium or non-reactive transport of solute from the source to the precipitation site under net fluid fluxes, which are several orders of magnitude lower than previously interpreted. Slow regional devolatilization events are dispersion-dominated, and promote solute redistribution on kilometer scale, hence, in the limiting case, require no advective fluid flux.

**Keywords.** reactive fluid flow, hydrothermal alteration, transport theory, mass conservation, fluid flux, fluid focusing

## 1 Introduction

Formation of economic hydrothermal mineralization is a product of efficiency of fluid focusing into and extent of chemical reactivity at the site of mineralization. These processes are reconstructed from petrological record, in particular alteration zoning, its intensity and extent, which yields an estimate of the time-integrated fluid flux (Ferry and Dipple 1991; Dolejš and Manning 2010; Ague 2014). An essential step in this procedure is an appropriate solution to mass-conservation transport equation, which contains additive contributions from advection of chemical species by fluid in or out of equilibrium with host rocks, and from lateral dispersion and diffusion effects (Ague 1998; Philpotts and Ague 2009). These phenomena operate on different length and time scales but may in turn provide insight into dynamics such as flow, diffusion and rates or continuous vs. episodic evolution of hydrothermal systems.

In this contribution, we identify and discuss several genetic types of hydrothermal systems: equilibrium-advective, disequilibrium-advective and dispersion-

diffusion styles, and demonstrate the heuristics and pitfalls of interpreting their alteration record.

## 2 Definitions

Hydrothermal alteration and veining are net results of replacement and/or precipitation reactions. The extent of reaction, hence the intensity of alteration, are directly related to the magnitude of disequilibrium at the alteration site. The extent of reaction between the hydrothermal fluid and the host environment is determined by: (i) overall pressure and temperature gradient along the fluid flow path under continuous local equilibrium, (ii) infiltration from a distinct environment where the fluid was sourced (temperature, pressure, distinct lithology) thus inducing disequilibrium, and (iii) variations inside the system of interest, which induce transport by dispersion and/or diffusion. Hydrothermal systems dominated by each of these three mechanisms have been described previously, but virtually no attempts were presented to illustrate on what scales these mechanisms may interfere and how they bias our estimates of fossil fluid fluxes.

## 3 Theory

Consider control volume of interest subject to the mass conservation (e.g., Steefel and Maher 2009):

$$\frac{\partial(\phi c_i)}{\partial t} = -v \frac{\partial(\phi c_i)}{\partial x} + D \frac{\partial^2(\phi c_i)}{\partial x^2} + \phi R_i, \quad (1)$$

where  $c_i$  is solute concentration ( $\text{mol m}^{-3}$ ),  $R_i$  is the reaction rate ( $\text{mol m}^{-3} \text{s}^{-1}$ ),  $v$  is the flow rate ( $\text{m s}^{-1}$ ),  $D$  is the combined diffusion-dispersion coefficient ( $\text{m}^2 \text{s}^{-1}$ ),  $\phi$  is porosity. Assuming equilibrium or steady state, that is, a time-invariant concentration of solute in the fluid, the right-hand side of Eq. (1) is equal to zero. Since alteration zoning represents a net result over duration of the hydrothermal event, the time-integrated mass-balance constraint becomes:

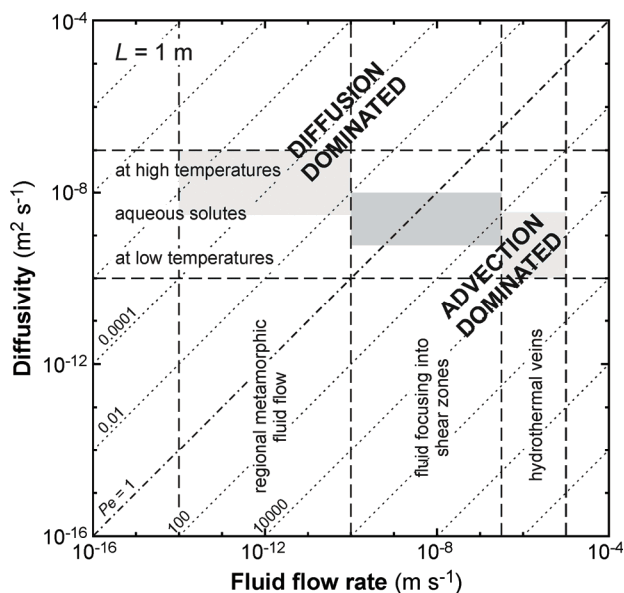
$$0 = -L \frac{\partial(\phi c_i)}{\partial x} + A \frac{\partial^2(\phi c_i)}{\partial x^2} + \phi c_i, \quad (2)$$

where  $L$  is the length scale of alteration and  $A$  represents the characteristic area of diffusion and dispersion. Two limiting approaches are conventionally used to interpret the observed mass changes in the alteration domain: (i) the solute mainly originates outside the alteration site and has been introduced by advection (dispersive transport is negligible), or (ii) the material is of local

origin and has been redistributed internally (advection by the fluid is negligible). As a consequence, the first approximation provides the maximum estimate of the time-integrated fluid flux, whereas the second approach requires no fluid flux to explain the observed alteration or vein-selvege sequence. Any limiting or intermediate situation of interest can be quantified by the Péclet number,

$$Pe = \frac{vL}{D}, \quad (3)$$

which reaches zero in the diffusive-dispersive systems, and approaches infinity in the advective systems (Fig. 1).



**Figure 1.** Advection- vs. dispersion-dominated hydrothermal systems as a function of fluid flow rate and solute diffusivity for a characteristic length scale,  $L = 1$  m. Contours are shown for Péclet number,  $Pe$ . Gray fields illustrate (i) low-temperature hydrothermal veins, (ii) focusing of medium-temperature fluids into appropriate structures such as shear zones, and (iii) dispersed regional metamorphic fluid flow. For this spectrum of processes, the alteration products and/or vein precipitates change from advection-dominated (hence externally derived) to diffusion-dominated (sourced locally). Data ranges: Thompson (1997), Oelkers (1997).

We now explore how these two limiting approximations affect the estimates and interpretation of the fluid flux in various hydrothermal settings.

#### 4 Dispersive hydrothermal systems

Chemical dispersion in a general sense includes any local redistribution of the solute. Longitudinal dispersion and diffusion is responsible for redistribution of solute along the flow path and, consequently, leads to the formation of diffuse geochemical fronts and alteration zones (Agué 1998, 2014). Transverse diffusion may provide significant additional source or sink for chemical constituents, hence, adversely affects or even precludes retrieval of the fluid flux. In the limiting case, the precipitation products originate from immediate surroundings and were formed in a stagnant pore fluid (no fluid flux). This mechanism is characteristic for

Alpine-style mineralization and numerous vein assemblages in metamorphic terrains (e.g., Widmer and Thompson 2001), where their formation by dissolution-precipitation is most likely assisted by transient gradients in a stress field.

The dynamics of a diffusive/dispersive system can be described by the Damköhler II number,

$$Da_{II} = \frac{kL^2}{D}. \quad (4)$$

For  $Da_{II} \gg 1$ , reaction times are much faster than diffusion time scales. In this case, local equilibrium is achieved over a length scale,  $L$ . The most significant variation in  $Da_{II}$  is expected to stem from quantities, which vary exponentially with environmental factors. Since the reaction rate ( $k$ ) and diffusivity ( $D$ ) both depend on temperature exponentially in an Arrhenian manner, the low- and high-temperature hydrothermal systems are expected to be discriminated by the Damköhler number effectively if the two activation energies are substantially different. Additionally, the reaction rate is a non-linear function of the driving force for dissolution or precipitation, hence magnitude of pressure fluctuations can be quantified by  $Da_{II}$  as well.

For quantitative characterization of the net alteration record of a diffusive/dispersive system, Eq. (2) reduces to

$$-\phi A \frac{\partial^2 c_i}{\partial x^2} = \phi c_i, \quad (5)$$

where the right-hand side represent the extent of reaction or mole amount of alteration products in the system (rock), and the porosity-area scale product,  $\phi A$ , on the left-hand side has the dimension of time-integrated fluid volume per distance, a prospective quantitative description of dispersive systems.

#### 5 Advective hydrothermal systems

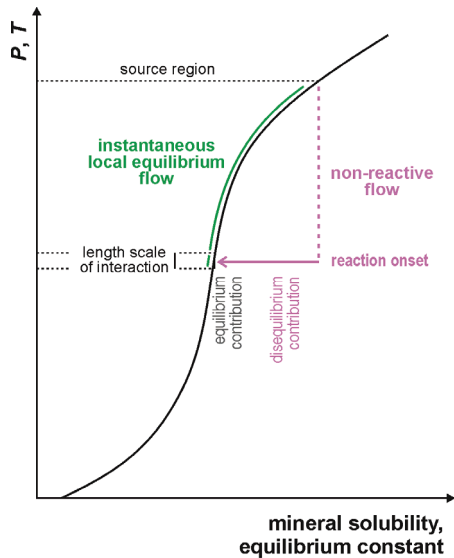
Advection-dominated hydrothermal systems are characterized by a limited extent of chemical transport by diffusion or dispersion with respect to the size of the system. This restriction can independently arise from (i) short duration of the hydrothermal event, or (ii) very small porosity in a transverse direction. In this case, Eq. (2) becomes:

$$\phi L \frac{\partial c_i}{\partial x} = \phi c_i, \quad (6)$$

where the right-hand side represent extent of reaction or mole amount of alteration products in the system (rock), and the porosity-length scale product,  $\phi L$ , on the left-hand side has the dimension of time-integrated fluid flux. The alteration record can thus be converted into the fluid flux provided that the change in concentration over distance is known.

In the advection-dominated systems, chemical reaction can be induced by two unrelated mechanisms: (i) temperature- and/or pressure-gradient, which affects solute-mineral equilibria along the flow path, or (ii) solute-mineral disequilibrium when a fluid enters the

system. The first approach applies to slow fluid flow rates (e.g., dispersed metamorphic fluid flow) and settings with negligible variation in the host lithology, whereas the second one is characteristic for fast, possibly variable fluid flow rate, and promoted by changes in host rock lithologies (Fig. 2).



**Figure 2.** Schematic illustration of different reaction extent produced in the alteration site during local-equilibrium flow (green) and disequilibrium infiltration (purple). Based on the pressure-temperature dependence of solute-mineral equilibria, the alteration record at the mineralization (interaction) site is expected to be different.

In order to address the significance of local equilibrium *vs.* disequilibrium infiltration in a continuous model, the concentration gradient in Eq. (6) is recast into:

$$\frac{\partial c_i}{\partial x} = \frac{\partial c_i}{\partial T} \frac{\partial T}{\partial x} + \frac{\partial c_i}{\partial P} \frac{\partial P}{\partial x} + \frac{\partial c_{i,diseq}}{\partial x} . \quad (7)$$

As shown by Dolejš and Manning (2010), the derivatives of concentration by temperature or pressure are linked to the standard thermodynamic properties of solute-mineral reactions (e.g., precipitation), as follows:

$$\frac{\partial c_i}{\partial T} \approx K \cdot \frac{\partial \ln K}{\partial T} = K \cdot \frac{\Delta_r H^\circ}{RT^2} , \quad (8)$$

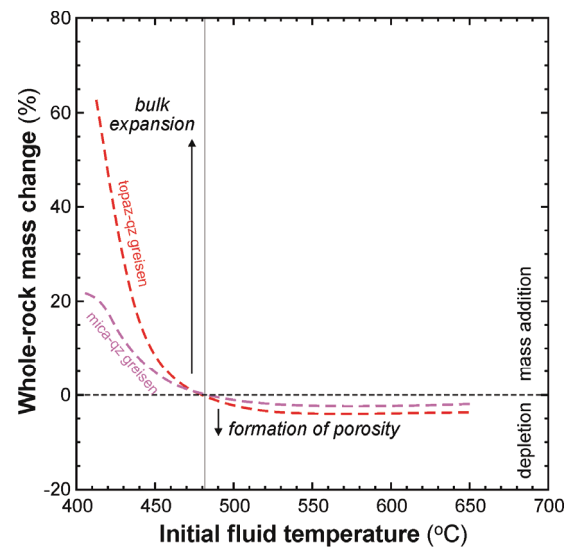
and

$$\frac{\partial c_i}{\partial P} \approx K \cdot \frac{\partial \ln K}{\partial P} = -K \cdot \frac{\Delta_r V^\circ}{RT} , \quad (9)$$

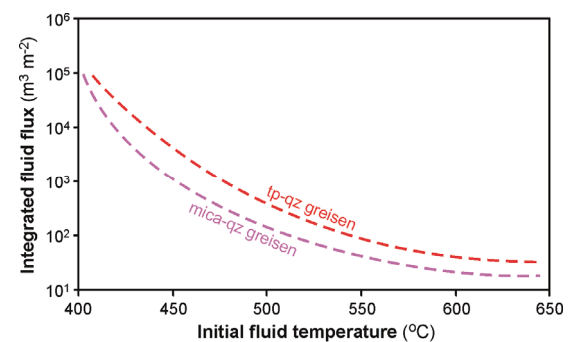
where the equilibrium constant ( $K$ ), the standard reaction enthalpy ( $\Delta_r H^\circ$ ) and volume ( $\Delta_r V^\circ$ ) refer to mineral dissolution equilibrium. Importantly, because mineral solubility gradients under typical *regional* geotherms are fairly constant, the system behavior is dominated by *absolute solubility* of mineral gangue of interest (e.g., quartz, calcite etc.), whereas during isobaric or upper-crustal fluid flow, the gradients terms (standard reaction enthalpy and volume in Eqs. 8 and 9) become predominant. This underlies, to name one example, the origin and interpretation of retrograde solubility.

Relative magnitudes of the equilibrium *vs.*

disequilibrium contributions are expected to vary widely in nature but have not been addressed before. To illustrate, we explore continuous transition from the equilibrium to disequilibrium behavior in a tin-mineralized greisen alteration in the Western Krušné hory/Erzgebirge pluton (Heřmanská and Dolejš 2013). In Figs. 3 and 4, the fluid flow through cooling intrusion into the greisenization site (400 °C, 500 bar) under continuous local equilibrium with the host granite represents the limiting case of the model (left-hand side). Additional reaction and mass change effects are expected, when the fluid infiltrated (rapidly) from a high-temperature source without equilibrating along its flow path. This scenario is bracketed by maximum source temperature of 650 °C at 1 kbar, corresponding to the granite solidus. Any likely intermediate situation has profound effects on alteration style, reaction-porosity formation feedback (Fig. 3) and, through Eq. (7), on the estimated time-integrated fluid flux (Fig. 4).



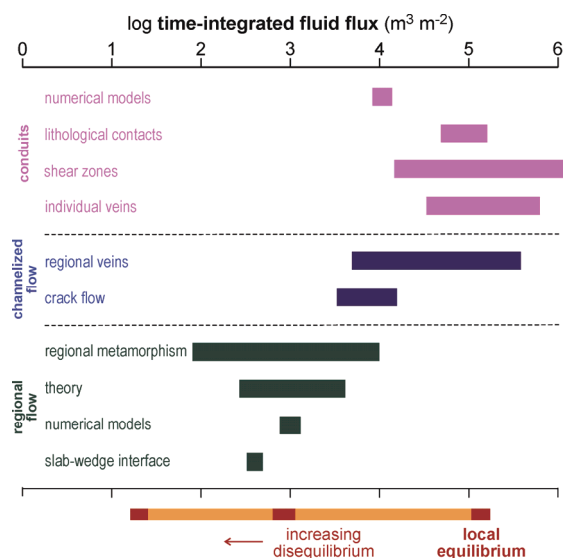
**Figure 3.** Whole-rock mass changes and porosity evolution during greisen alteration as a function of the initial temperature of infiltrating fluid, reaching equilibrium at the alteration site.



**Figure 4.** Time-integrated fluid flux necessary to reproduce the greisen alteration as a function of the initial temperature of infiltrating fluid.

The model example of the tin-mineralized greisens from the Western Krušné hory/Erzgebirge pluton illustrates that disequilibrium upon fluid infiltration strongly dominates the process and, as a consequence, the estimate of the time-integrated fluid flux may be biased by several orders of magnitudes. This range is comparable to fluid fluxes previously described worldwide

(Fig. 5). This example illustrates the urgent need for careful consideration of individual contributions in Eq. (7). General persistence of disequilibrium infiltration in numerous proximal magmatic-hydrothermal settings requires strong variations in the Damköhler number along the flow path, whose origins are still unknown.



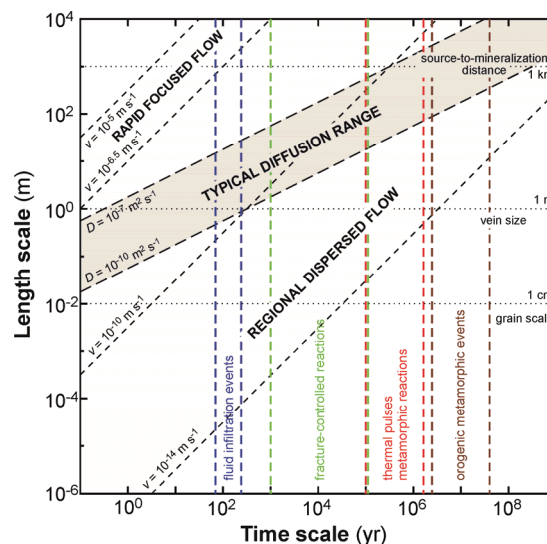
**Figure 5.** Time-integrated fluid fluxes in diverse geological settings (Ague 2014) compared to variability in the flux estimate during disequilibrium infiltration and formation of greisen alteration (bottom).

Interpreting individual factors driving the extent and scales of alteration reactions requires applying the general system factors (such as time scales) to individual mass transport mechanisms to evaluate their length scales (Fig. 6). During rapid hydrothermal events ( $\sim 10^2$  yr), the characteristic diffusion distances remain comparable to the vein thickness, but maximum-known flow rates are capable of transporting chemical constituents on kilometer scale. The net fluid fluxes may remain low, because alteration reactions are effectively driven by disequilibrium. By contrast, during regional pervasive fluid flow accompanying metamorphic devolatilization events ( $\sim 10^7$  yr), the diffusion and dispersive distances substantially increase and become sufficient to redistribute material on kilometer scale internally. In a limiting case, the transport can appear in a stagnant medium under external (pressure, temperature) gradients at zero fluid flux.

## 6 Concluding remarks

Understanding the dynamics and reaction mechanisms in hydrothermal systems requires coupling between environmental factors (e.g., time scale of hydrothermal event or fluid flow rate), observables (e.g., length scale of alteration or mineralization), intrinsic properties of the system (e.g., reaction rates or chemical diffusivity), which can be linked by a small number of quantitative descriptors (e.g., Péclet or Damköhler number). Constructing a general factor-oriented classification scheme of hydrothermal systems, which would incorporate these quantitative descriptors should facilitate identification of the principal driving forces

from geological record. These should, in principle, address the causal relationships between length scales (sizes) of metal sources and accumulations and the time and reactivity scales necessary for their transport.



**Figure 6.** Time scales vs. length scales of hydrothermal events and their products (see text for discussion). Data ranges: Oelkers (1997), Ague (2014).

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