The Importance of Vein Selvaging in Controlling the Intensity and Character of Subsurface Alteration in Hydrothermal Systems

L. M. Cathles

Department of Geological Sciences, 2358 Snow Hall, Cornell University, Ithaca, New York 14853

Abstract

The identity and abundance of secondary minerals produced when a hydrothermal fluid, initially in equilibrium with its host formation, is or can be expelled down a temperature gradient toward the surface, is strongly influenced by the compositions of hydrothermal solutions found in many natural hydrothermal systems (Cathles, 1986; see also Gigenbach, 1981, 1985).

A hydrothermal fluid is assumed to be in equilibrium with the mineral buffer in the source region. The source region might be an intimately fractured region at the margin of an intrusion, or porous rocks or sediments undergoing metamorphism. These initially equilibrated fluids are assumed to move up toward the surface in one of two contrasting styles: either the fluids move upward slowly through a densely fractured rock or porous and uniformly permeable sediment in such a way as to maintain equilibrium with the full set of original buffer minerals, or the fluids enter a selvaged vein and move to the surface shielded from further chemical interaction with any host-rock mineral. A vein might be selvaged or sealed by diffusive chemical interaction with the host rock by early precipitation of quartz or calcite. The selvaged case would also persist if the host-rock minerals were nonreactive. In both the selvaged and fully buffered cases alteration occurs in the sense that minerals are precipitated or replaced, but not in the sense that we are computing the grams of new (precipitated or replaced) hydrothermal minerals per gram of original host rock. If we are thinking of a hydrothermal solution. Alteration is thus used in this paper in a somewhat unusual way. Here the term alteration applies both to the precipitation of gangue minerals in a vein and to precipitation or replacement of minerals outside the vein. The alteration in both cases is driven by a flux of chemical species from the hydrothermal solution to rock minerals. The chemical flux is determined by requiring local equilibrium with a set of mineral buffers in one case and by mandating mineral precipitation until the solution is saturated or undersaturated with respect to all buffer minerals in the other (selvaged) case. In the selvaged case, conservation of chemical mass requires that the total flux of some chemical species into a volume element enclosing a set streamlines (flow tube), $Q_{\text{TOT}}$, minus the total chemical flux of $x$ at some distance downstream, $Q_{\text{TOT}}$, equal the addition of chemical component $x$ to the rock volume element, $V_{\text{R}}$.

The Model

At depth, fluids heated by an intrusion or in the earth's normal thermal gradient are assumed to equilibrate with the following nine buffer minerals: quartz, calcite, fluorite, albite, muscovite, spodumene, maximum microcline (K-feldspar in this paper), K-feldspar, pyrite, and magnetite. The chemistry of the hydrothermal fluid at such a buffer depends only on temperature, total CT moleality, and pressure. Oxygen and sulfur fugacity, pH, etc., are determined by the mineral buffer. It has been previously shown that, using a slightly modified QS3/6 thermodynamic data base, the calculated solution compositions in equilibrium with this buffer correspond well to the compositions of hydrothermal solutions found in many natural hydrothermal systems (Cathles, 1986; see also Gigenbach, 1981, 1985).

A hydrothermal fluid is assumed to be in equilibrium with the mineral buffer in the source region. The source region might be an intimately fractured region at the margin of an intrusion, or porous rocks or sediments undergoing metamorphism. These initially equilibrated fluids are assumed to move up toward the surface in one of two contrasting styles: either the fluids move upward slowly through a densely fractured rock or porous and uniformly permeable sediment in such a way as to maintain equilibrium with the full set of original buffer minerals, or the fluids enter a selvaged vein and move to the surface shielded from further chemical interaction with any host-rock mineral. A vein might be selvaged or sealed by diffusive chemical interaction with the host rock by early precipitation of quartz or calcite. The selvaged case would also persist if the host-rock minerals were nonreactive. In both the selvaged and fully buffered cases alteration occurs in the sense that minerals are precipitated or replaced, but not in the sense that we are computing the grams of new (precipitated or replaced) hydrothermal minerals per gram of original host rock. If we are thinking of a hydrothermal solution. Alteration is thus used in this paper in a somewhat unusual way. Here the term alteration applies both to the precipitation of gangue minerals in a vein and to precipitation or replacement of minerals outside the vein. The alteration in both cases is driven by a flux of chemical species from the hydrothermal solution to rock minerals. The chemical flux is determined by requiring local equilibrium with a set of mineral buffers in one case and by mandating mineral precipitation until the solution is saturated or undersaturated with respect to all buffer minerals in the other (selvaged) case. In the selvaged case, conservation of chemical mass requires that the total flux of some chemical species into a volume element enclosing a set streamlines (flow tube), $Q_{\text{TOT}}$, minus the total chemical flux of $x$ at some distance downstream, $Q_{\text{TOT}}$, equal the addition of chemical component $x$ to the rock volume element, $V_{\text{R}}$.

The model requires that the total flux of some chemical species through the flow tube is equal to the addition of chemical component $x$ to the rock. The chemical flux is determined by requiring local equilibrium with a set of mineral buffers in one case and by mandating mineral precipitation until the solution is saturated or undersaturated with respect to all buffer minerals in the other (selvaged) case. In the selvaged case, conservation of chemical mass requires that the total flux of some chemical species into a volume element enclosing a set streamlines (flow tube), $Q_{\text{TOT}}$, minus the total chemical flux of $x$ at some distance downstream, $Q_{\text{TOT}}$, equal the addition of chemical component $x$ to the rock volume element, $V_{\text{R}}$.

The flux of basis species to the rock is related to the mineral alteration of the rock:

$$\Delta M_{\text{molar}} = (S)^{-1}F_x$$

where $\Delta M_{\text{molar}}$ is the molar of the jth new (hydrothermal) buffer mineral precipitated or dissolved per unit volume within the tube by the flux of basis species $i$ from the hydrothermal fluid, and $(S)^{-1}$ is the inverse of the transposed stoichiometric matrix expressing the composition of the buffer minerals j in terms of the basis species i. The mineral alteration can be expressed as the weight fraction of the jth hydrothermal mineral precipitated or dissolved by modifying $\Delta M_{\text{molar}}$:

$$\Delta M_{\text{molat}}(\text{wt}) = \frac{\Delta M_{\text{molar}}}{W_{\text{molar}}},$$

where $W_{\text{molar}}$ is the molecular weight of buffer mineral j, and, d is the density of the rock in the flow tube.

If the mass flux through the tube is composed of liquid and vapor (i.e., the hydrothermal fluid is boiling) and the fluid remains in equilibrium with the full initial suite of buffer minerals, equation (2) is modified:

$$F_{\text{molat}}(c) = \frac{Q_{\text{molat}}(c)}{W_{\text{molar}}(c)}$$

where $F_{\text{molat}}(c)$ is the molar of basis component i per kilogram of the liquid phase, $Q_{\text{molat}}(c)$ is the total chemical flux of $c$ at some distance downstream, $W_{\text{molar}}(c)$ is the molecular weight of buffer mineral j, and $c$ is the concentration of chemical basis species i (e.g., the concentration of the species itself plus the concentration of all aqueous complexes that contain the species) in moles per kilogram. The basis species are the minimum number of building blocks from which the solution complexes and buffer minerals can be constructed and thus described. A set of elements could be used, but it is convenient and conventional that a set of solution species be selected instead. The basis set we select is: Ca, Mg, Na, K, Mg, Al, Si, Fe, Mn, Fe, Ni, Cu, Zn, and H2O. Thus in terms of the above notation $C_{\text{Ca}}$ is the total concentration of Ca2+ in solution, and $C_{\text{Na}}$ is the concentration of Ca2+ ion in solution in moles per kilogram.

Noting that $Q_{\text{molat}}(c) = Q_{\text{molat}}(c) = Q_{\text{molat}}(c)$, the flux of basis species to the rock in equation (1) may be reexpressed:

$$F_{\text{molat}}(c) = Q_{\text{molat}}(c)/W_{\text{molar}}(c).$$

where $W_{\text{molar}}$ is the molecular weight of buffer mineral j, and, d is the density of the rock in the flow tube.
The liquid and vapor are assumed to be locally in equilibrium, the composition of the vapor is calculated from that of the liquid using the gas dissolution log K values in the EQ3/6 data base. These log K values are in good agreement with Drummond and Obomo's (1985) Henry's law relations for T = 300°C. The gas species considered in our calculations are CO2, H2, H2O, and H2S (or H2O, steam). We do not consider CH4 or SO2. The latter is unimportant because of the reduced nature of the boiling fluid. Note that equation (5) reduces to equation (2) when y = 1 everywhere (no boiling). Thus equations (3), (4), and (5) are the relations required to describe alteration in cases where the fluid maintains chemical contact with the host minerals.

Horizontal losses of heat are assumed to be negligible and thermal steady state is assumed, so y is determined by conservation of energy as a simple function of the temperature at the base of the boiling zone, Tb, and the temperature at the site, T, where: 

\[ T(T) = k(T) + Q(T) + y(T) \] 

Here, k is the enthalpy of liquid (l) or vapor (v) which is available in simple polynomial form in Elder (1981). The chemical composition of a fluid in equilibrium with the full suite of rock buffer minerals and the initial (source region) composition of the fluid were calculated using an equilibrium solver code similar to EQ3 (Cathles, in prep; see also Cathles, 1986, for an example of the use of EQ3 to solve for buffered solution composition). In these calculations, the full EQUERRA geochemical data base (Wolery, 1983) was modified as described by Cathles (1986) was used. Thus, for example, the calculations consider the competition that solutions competing to the total basis species concentration, Cb. The log K values describing the dissolution of the buffer minerals to basis species are at EQ3/6 data base. For evolved veins the upward-migrating fluid is incrementally boiled as indicated in equation (6). As show in this work, the composition of the liquid at T in determined from its composition at T by extracting the volatile components and increasing the concentration of the nonvolatile species in the liquid appropriately:

\[ C_b(T_b) = \frac{C_b(T)}{1 - \Delta y} \]  

Where, \( \Delta y = y(T_b) - y(T) \) supersaturated buffer minerals are then precipitated at T until all are just saturated by a method briefly described below. The change in liquid composition is then:

\[ \Delta C_b = C_b(T_b) - C_b(T) \text{(calc)} \]  

Where C_b(T) is given in equation (6) and is the total basis species composition of the liquid phase before precipitation of the supersaturated mineral phases and C_b(T)_calc is the composition after precipitation. The chemical flux from the liquid phase to the rock is then given by:

\[ F_r = \frac{y(T_b) + y(T)}{2} \Delta C_b \text{(calc)} \]  

Where \( \Delta C_b \text{(calc)} \) is from equation (7). Note that if y = 1 everywhere (no boiling), equation (5) reduces to (2). The added factor simply accounts for the reduction of the liquid phase as boiling progresses in a fashion analogous to that of equation (5), which also reduces to equation (2) if y = 1 everywhere.

Equation (8) is approximate in that it assumes that the change in vapor composition is complete between T and T_b. There is an insignificant impact on the chemical flux from the liquid to the vapor phase compared to the flux that occurs at constant vapor composition, as a result of the increase in the fraction of water that is vapor at T. The approximation leads to about a 20 percent underestimation of alteration, which is not a significant error for our present purposes. It is a small price to pay for a vast simplification in the calculations. A more precise calculation of C_b(T, T_b) for each plume is possible, but 3.95 x 10^4 g of veined calcium veins is a close approximation of the chemistry of the fluid in this temperature range by the boiling veined curve in Figure 2.

The situation is mineralogically more complex if boiling occurs and volatiles are fractionated into the vapor phase, but the intensity of alteration is about the same. Figure 3 shows the proportion of alteration requires precipitation with the precipitation of K-feldspar and pyrite precipitated between 300°C and 267.5°C. Beware that the exponential scale emphasizes the importance of short phases. Figure 2 shows the intensity of alteration (as measured by the mass of hydrothermal minerals precipitated per gram of original rock for a 1 g/cm^3 hydrothermal flux through the tube, Q). Our purpose is to investigate variations in the intensity of alteration caused by the presence or lack of a single mineral for constant T, T_b, and Q. In all calculations Q = 1 g fluid/cm^3 rock, 267°C = 100 k, and p_v = 2.7 g/cm^3. Results of Calculations

The results of the calculations described above are given in Figures 1 to 5. Consider first precipitation caused by simple boiling in a veined vein. Figure 1 shows that the boiling, veined case only quartz and muscovite need to precipitate in order to keep all buffer minerals saturated or undersaturated. As can be seen, only minor amounts of muscovite precipitate compared to quartz. Figure 2 shows the amount of quartz and muscovite precipitate as a function of temperature. The amount of quartz precipitate is just what would be expected. For example, the solubility of quartz at 300°C and 267°C is 584 and 485 ppm, respectively, so that 3.95 x 10^4 g of veined calcium veins is precipitated from each gram of hydrothermal fluid cooled 1°C. At a throughput of 1 g fluid/cm^3 and a rock density of 2.7 g fluid/cm^3, the throughput is 1.27 g fluid per g rock, so the rock alteration between 300°C and 267°C is expected to be (1/2.7) X 3.95 x 10^4 = 1.46 x 10^-3 g/cm^3 of vein/min, which is the value indicated in this temperature range by the boiling veined curve in Figure 2.

A dramatic change in the nature and intensity of hydrothermal alteration occurs if the upwelling hydrothermal fluids maintain chemical contact with the buffer minerals. Figure 4a and b shows the proportions of new minerals produced if a nonboiling or boiling hydrothermal solution moves down a temperature gradient while maintaining chemical equilibrium with the full set of buffer minerals that initially determined its chemical composition. Figure 2 shows that the mass of new minerals produced per mass of original rock in these fluid-rock equilibrium cases is more than three orders of magnitude greater than in the veins cases previously discussed.
Increase in alteration intensity comes from the dissolution of buffer minerals not shown in the diagrams. This dissolution brings about the large increase in the mass of new (precipitated or replaced) minerals.

Finally, note that the pressure gradient in most boiling hydrothermal systems is close to cold-water basaltic for reasons discussed by Elders (1966). We can convert the temperature profile in Figure 4 to depth and replot the result in Figure 5. Figure 5 emphasizes the effects of the nonlinear temperature gradient probable in hydrothermal systems, whether boiling or not, and provides a more realistic picture of the alteration suggested by the simple models adopted in this paper.

Discussion and Conclusions

Approximations have been made in the above analysis which deserve brief discussion. Q is assumed to be constant throughout the geothermal system. This requires constant rock permeability. Of course permeability may vary strongly with subsurface location, leading to the strong concentration of flow in certain areas or in certain vein intervals. Thus parts of a geothermal system may experience much higher values of local Q than others, and the intensity of alteration as a function of depth at any location will be lumpy (as every explorationist knows) rather than smooth as shown in Figure 2. Conservation of fluid mass requires, however, that the total (average) alteration in upwelling zones obey the smooth (average) relations in Figure 2. Alteration averaged over broad horizontal surfaces of increasing depth should approximate the alteration depth intensity curves in Figure 3, provided local chemical equilibrium is maintained.

A particular set of mineral buffers has been chosen and other minerals which might be supersaturated with respect to solutions in equilibrium with this buffer have been ignored. This is different from the usual EQ/3 approach where no mineral in the data base is allowed to be super- or undersaturated. Some (e.g., Giggenbach, 1981, 1985b, this paper) consider it important to have the freedom to select a particular mineral buffer and ignore other mineral phases which, for reasons of kinetics, mineral stoichiometry, or erroneous thermodynamic data, do not react in nature as thermodynamically expected. This freedom has been exercised here with respect to methane, which could have been but was not included as a gas phase, and in the selection of the buffer minerals. Others believe it better to automatically select the most unstable set of buffer minerals. While defending the general approach taken here, it is admitted that the particular buffer choices may not be the best one in all cases. It produces geologically interesting alteration profiles (see Figs. 4 and 5). Deep K Feldspar-Ca-Al silicate (potassic) alteration oversteps by quartz-muscovite alteration is a common association. Gold mineralization is often associated with muscovite, quartz, and calcite. The mean age of muscovite alteration in Figure 4 is geologically intriguing. It must be remembered, however, that at these shallow depths (Fig. 5) vapor condensation and oxidation commonly generate acids that produce an advanced argillic alteration. Our model has no conduction term and does not accommodate either near-surface condensation or oxidation. The alteration calculated here is therefore not claimed to be necessarily realistic; the alteration models are not applied to any particular geothermal system in this paper.

The purpose of the calculations is different. They are designed to illustrate the changes in alteration character and intensity caused by vein selvaging. Figure 2 shows that vein selvaging reduces the intensity of alteration at constant fluid throughput by three orders of magnitude. The reduction is important because the intensity of alteration is often (consciously or unconsciously) used by explorationists as a measure of the amount of hydrothermal throughput and exploration potential of an area. The calculations show that in fact a selvaged vein system with 10 times less alteration minerals may have in fact transmitted 100 times more fluid than a nonselevaged system with the same mass of hydrothermal minerals.

The end-member selvaged and fully buffered equilibrium models are of course idealized. In nature it is most likely that a system moving through fractures will be in at least slight chemical disequilibrium with the surrounding host rock and that there will be some diffusion-controlled chemical exchange with the host. Some gangue minerals will be precipitated in the vein, and some alteration (by replacement or precipitation) will occur in the host rock. The diffusive chemical flux from the host rock will cause different minerals to be precipitated in the vein, and the diffusive chemical flux from the vein may change mineral alteration in the host rock. Only in the case that the fractures are so close together that the halos overlap will the equilibrium case considered above fully prevail. Only when the sides of the fractures are completely sealed by mineral precipitates in such a way that there is no diffusion into the host rock will the selvage case discussed above fully persist. Even then kinetics may not allow rapid enough mineral precipitation to maintain complete chemical equilibrium.

More realistic intermediate cases that take into account diffusive fluxes and chemical kinetics will certainly differ from the simple end-member cases we present. However, the very large (10,000) difference in new mineral formation per unit fluid throughput between the selvaged and nonselevaged (fully buffered) cases and the very different mineralogy and depth dependence of the alteration suggests that selvaging must be carefully taken into account in assessing the exploration implications of alteration. It is unlikely that more refined models (the inclusion of diffusion or chemical kinetic control on the rate of reactions, for example) or different chemical assumptions (a choice of different buffer minerals, for example) will significantly change the basic conclusion that selvaging has a surprisingly large influence on the intensity and character of mineral alteration in hydrothermal systems.

Acknowledgments

The author would like to thank Ted Appleyard and Jayanta Guha for organizing the conference and proceedings that motivated the preparation of this paper. Two helpful reviews were received from Economic Geology reviewers.

REFERENCES


