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

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Abstract

The identity and abundance of secondary minerals produced when a hydrothermal fluid, initially in equilibrium with its host formation, convects or is otherwise propelled down a temperature gradient toward the surface are calculated with and without boiling. The calculations show that the mass of secondary minerals produced by a unit throughput of hydrothermal water is surprisingly dependent on selvaging. Mineral precipitation is over 1,000 times greater when chemical contact is maintained with the host formation than when the upwelling fluid is chemically isolated from the host rock by selvages. This means, for example, that a selvaged vein with only one-tenth the hydrothermal mineral alteration of a nonselvaged vein formed in a similar environment may nevertheless have transmitted over 100 times more hydrothermal fluid and precipitated 100 times the mass of ore minerals. These conclusions are for end-member equilibrium models. The magnitude of the effect suggests, however, that selvage formation will remain an important consideration in cases between the two end-member extremes and for cases subject to kinetic control.

Introduction

MANY ore deposits form near the surface where boiling, strong cooling, or both cause metals to precipitate from upwelling hydrothermal fluids. A fundamental problem in mineral exploration is the interpretation of the alteration associated with these processes in terms of the exploration potential of an area. Simple calculations presented here show that the intensity of alteration per unit fluid throughput surprisingly is strongly dependent on the extent to which the upwelling fluid remains in chemical contact with the host rock. Since the mass of metals deposited in any system is necessarily related to the fluid throughput but not necessarily to alteration, the effects of vein selvage formation must be considered when evaluating the exploration potential of an area.

The calculations presented are deliberately simplified and designed to specifically address the effects of selvage formation in boiling and nonboiling systems. The geologic setting is assumed to be deep enough that vapor condensation, atmospheric oxidation, or the drainback of acid waters from the surface are not factors. Advanced argillic alteration is not considered.

Local fluid-rock equilibrium is assumed. Pore fluids in the crust are generally in chemical equilibrium with the common inorganic rock minerals they contact (e.g., Ellis, 1970; Reed and Spycher, 1984). The chemistry of the rock-buffered pore fluid is not very sensitive to the particular aluminosilicate minerals contacted. It is for these two reasons that the temperature of a geothermal system can be inferred from analyses of fluid composition of its fluids through the application of various geothermometers (e.g., Na-K-Ca, SiO₂, and various gas geothermometers; Henley et al., 1984). Pore fluids may equilibrate at temperatures as low as 50°C under common (relatively quiescent) crustal flow conditions. Local fluid-mineral equilibrium is thus probably a reasonable assumption in many hydrothermal systems, even ones where flow is concentrated in fractures, but an additional consideration in the interpretation of alteration must be whether the local equilibrium assumption is violated. This possibility should be kept in mind by readers of this paper.

Boiling in geothermal systems has been addressed by a number of previous studies. Excellent discussion has been given by Elder (1966, 1981). Donaldson (1968) formulated and solved the problem in a particularly elegant fashion. Recently some of the chemical consequences of boiling have been addressed. Drummond and Ohmoto (1985), for example, calculated metal precipitation in boiling geothermal systems. Bowers (1990) has made general calculations of chemical and isotopic alteration in boiling systems. There appear to have been no previous studies quantitatively addressing the effects of selvaging, however.

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, low albite, muscovite, wairakite, maximum microcline (K feldspar in diagrams in this paper), 14Å daphnite, pyrite, and magnetite. The chemistry of the hydrothermal solution in contact with such a buffer depends only on temperature, total Cl⁻ molality, and pressure. Oxygen and sulfur fugacity, pH, etc., are determined by the mineral buffer. It has been previously shown that, using a slightly modified EQ3/6 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 Giggenbach, 1981, 1988).

In our models, hydrothermal fluid is assumed to be in equilibrium with the mineral buffer in the source region. The source region might be an intimately fractured reaction zone at the margin of an intrusion or porous rocks or sediments undergoing metamorphism. These initially equilibrated fluids are assumed to move upward 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 from diffusive chemical interaction with the host rock by early precipitation of quartz or calcite. The selvaged case would also pertain 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. Alteration is quantified in this paper by computing the grams of new (precipitated or replaced) hydrothermal minerals per gram of original host for a unit throughput of 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 either case, conservation of chemical mass requires that the total flux of some chemical species i into a volume element enclosing a set streamlines (flow tube), $AQ[C_{\Sigma i}]_{in}$, minus the total chemical flux of i out of that volume element some distance Δx downstream, $AQ[C_{\Sigma i}]_{out}$, equal the addition of chemical component i to the rock volume element, VF_i:

$$VF_i[\text{moles } i/\text{cm}^3] = AQ[C_{\Sigma i}]_{in} - AQ[C_{\Sigma i}]_{out}. \quad (1)$$

A is the cross-sectional area of the flow tube in cm², $V = A\Delta x$ is the volume of the flow tube, Q is the fluid flux through the tube over some time interval in kg/cm², and $C_{\Sigma i}$ is the total 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 species list we select is: Cl⁻, Na⁺, K⁺, Ca⁺², Al⁺³, SiO₂(aq), HCO₃⁻, Fe⁺², Fe⁺³, HS⁻, H⁺, and H₂O. Thus in terms of the above notation $C_{\Sigma4}$ is the total concentration of Ca⁺² in solution, and C_4 is the concentration of Ca⁺² ion in solution in moles per kilogram.

Noting that $QA/V = Q'$ is the kilograms of hydrothermal solution passed through the flow tube per cm³ of rock enclosed, considering that the inlet and outlet ends of the tube are at temperatures T_1 and T_2, respectively, and denoting the difference between inlet and outlet total basis species concentration at the two ends by $\Delta^{T_1}_{T_2}C_{\Sigma i}$, the flux of basis species to the rock in equation (1) may be reexpressed:

$$F_i[\text{moles } i/\text{cm}^3] = Q'[\text{kg/cm}^3]\Delta^{T_1}_{T_2}C_{\Sigma i}. \quad (2)$$

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

$$\Delta M_j[\text{moles}/\text{cm}^3] = (S^T_{ji})^{-1}F_i, \quad (3)$$

where ΔM_j is the moles 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 $(S^T_{ji})^{-1}$ 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 may be expressed as the weight fraction of the jth hydrothermal mineral precipitated or dissolved by modifying ΔM_j:

$$\Delta M_j'[g_{alt}/g_{rk}] = \Delta M_j[\text{moles}/\text{cm}^3]W_j/\rho_r, \quad (4)$$

where W_j is the molecular weight of buffer mineral j, and ρ_r is the density of the rock in the flow tube.

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

$$F_i[\text{moles } i/\text{cm}^3]$$
$$= Q'[\text{kg/cm}^3]\Delta^{T_1}_{T_2}(yC^l_{\Sigma i} + (1-y)C^v_{\Sigma i}), \quad (5)$$

where $C^l_{\Sigma i}$ is the moles of basis component i per kilogram of hydrothermal solution in the liquid phase, $C^v_{\Sigma i}$ is the moles of basis component i per kilogram of hydrothermal solution in the vapor phase, and y is the fraction of total hydrothermal fluid flux in the liquid state at any location (temperature) along the 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 Ohmoto's (1985) Henry's law relations for $T \leq 300°C$. The gas species considered in our calculations are CO_2, H_2, H_2S, O_2, S_2, and H_2O (steam). We do not consider CH_4 or SO_2. The latter is unimportant because of the reduced nature of the boiling fluid. Note that equation (5) reduces to (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, T_b, and the temperature at the site, T: $h^l(T_b) = h^l(T)y + h^v(T)(1 - y)$. Here h is the enthalpy of liquid (l) or vapor (v) water 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 EQ3/6 thermodynamic data base (Wolery, 1983) as modified by Cathles (1986) was used. Thus, for example, the calculations consider the contributions of 43 solution complexes to the total basis species concentration, $C^l_{\Sigma i}$. The log K values describing the dissolution of the buffer minerals to basis species are also taken from the EQ3/6 data base.

For selvaged veins the upward-migrating fluid is incrementally boiled as indicated in equation (6). As shown by (6) the composition of the liquid at T_2 is determined from its composition at T_1 by extracting the volatile components and increasing the concentration of the nonvolatile species in the liquid appropriately:

$$C^l_{\Sigma i}(T_2) = \frac{C^l_{\Sigma i}(T_1)}{1 - \Delta y} + \Delta y C^v_{\Sigma i}(T_1), \qquad (6)$$

where $\Delta y = y(T_1) - y(T_2)$. Supersaturated buffer minerals are then precipitated at T_2 until all are just saturated by a method briefly described below. The change in liquid concentration is then:

$$\Delta^{T_1}_{T_2}C_{\Sigma i} = C^l_{\Sigma i}(T_2) - [C^l_{\Sigma i}(T_2)]^{equilibrium}, \qquad (7)$$

where $C^l_{\Sigma i}(T_2)$ is given in equation (6) and is the total basis species composition of the liquid phase before precipitation of the supersaturated mineral phases and $[C^l_{\Sigma i}(T_2)]^{equilibrium}$ is the composition after precipitation. The chemical flux from the liquid phase to the rock is then given by:

$$F_i = \left(\frac{y(T_1) + y(T_2)}{2}\right)Q'\Delta^{T_1}_{T_2}C_{\Sigma i}, \qquad (8)$$

where $\Delta^{T_1}_{T_2}C_{\Sigma i}$ is from equation (7). Note that if y = 1 everywhere (no boiling), equation (8) reduces to (2). The added factor simply accounts for the reduction of the liquid phase as boiling progresses in a fashion analogous to that in equation (5), which also reduces to equation (2) if y = 1 everywhere.

Equation (6) is approximate in that it assumes the change in vapor phase composition between T_1 and T_2 has 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_2. 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.

$C^l_{\Sigma i}(T_2)]^{equilibrium}$ was calculated from $C^l_{\Sigma i}(T_2)$ in the selvaged vein cases in the following fashion: The change in the logarithm of the saturation index of the Kth supersaturated mineral, $\partial \log I_K$, to the incremental removal of the stoichiometric equivalent of the Lth supersaturated mineral from solution, ∂C_L, was first calculated:

$$\frac{\partial \log I_K}{\partial C_L} = J_{KL}. \qquad (9)$$

The Jacobian was then used in a generalized Newton-Raphson iteration scheme to determine mineral precipitation required to reduce log I_K to zero for all supersaturated buffer minerals. At each iteration:

$$C^n_{\Sigma i} = C^{n-1}_{\Sigma i} - J^{-1}_{KL}I^{n-1}_K S_{iL}, \qquad (10)$$

where J^{-1}_{KL} is the inverse of the Jacobian matrix, S_{iL} is the stoichiometric matrix describing the composition of the Lth mineral in terms of the i basis species, and I^n_K is calculated initially ($n = 0$) from the fluid composition at T_1 at temperature T_2 and subsequently ($n \geq 1$) recalculated after subtracting the chemical increments removed by mineral precipitation. This scheme is similar to that employed in the well-known geochemical program EQ6, and as above the full EQ3/6 log K data base is used. It should be emphasized that precipitation in the selvaged calculations is limited to supersaturated buffer minerals and no dissolution is allowed. In all calculations the precipitation of minerals was calculated for 1°C increments, e.g., $T_1 - T_2 = -1°C$. Two iterations (e.g., $n \leq 2$) were found sufficient to reduce log I^n_i to less than 0.001 for all minerals.

In this paper, flow is assumed to be along the two-phase curve of water whether boiling occurs or not. It is then apparent from equations (5) through (7) that the intensity of alteration for a specified mineral buffer and specified T_1 and T_2 is related to the kilograms of hydrothermal fluid per unit volume that have passed

through the tube, Q'. Our purpose is to investigate variations in the intensity of alteration caused by the presence or lack of selvaging for constant T_1, T_2, and Q'. In all calculations $Q' = 1$ g fluid/cm³ rock, ΣCl^- = 1,000 ppm, and $\rho_r = 2.7$ g/cm³.

Results of Calculations

The results of the calculations described above are given in Figures 1 to 5. Consider first the precipitation caused by simple cooling in a selvaged vein. Figure 1 shows that in the nonboiling, selvaged 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 precipitated as a function of temperature. The amount of quartz precipitated is just what would be expected. For example, the solubility of quartz at 300° and 275°C is 586 and 488 ppm SiO_2, respectively, so that 3.95×10^{-6} g of SiO_2 is precipitated from each gram of hydrothermal fluid cooled 1°C. At a throughput of 1 g fluid per cm³ and a rock density of 2.7 g fluid per cm³, the throughput is 1/2.7 g fluid per g rock, so the rock alteration between 300° and 275°C is expected to be (1/2.7) $\times 3.95 \times 10^{-6} = 1.46 \times 10^{-6}$ $g_{SiO_2}/g_{/rock}$, which is the value indicated in this temperature range by the nonboiling selvaged 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 proportions of calcite, quartz, K feldspar, and pyrite precipitated between 300° and 267.5°C. Beware that the exponential scale emphasizes the importance of minor 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/cm³ hydrothermal flux

FIG. 2. The intensity of alteration for the cases shown in Figures 1, 3, 4, and 5 expressed as the grams of new hydrothermal minerals produced per gram of rock. The alteration per unit fluid throughput is over 1,000 times greater if the fluid and rock maintain chemical interaction than if the fluid is isolated from host-rock minerals by vein selvages.

between planes 1°C different in temperature) is a little larger initially but less later in the cooling. Boiling increases deep, at the expense of shallow, precipitation.

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 the 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 selvaged vein cases previously discussed. The
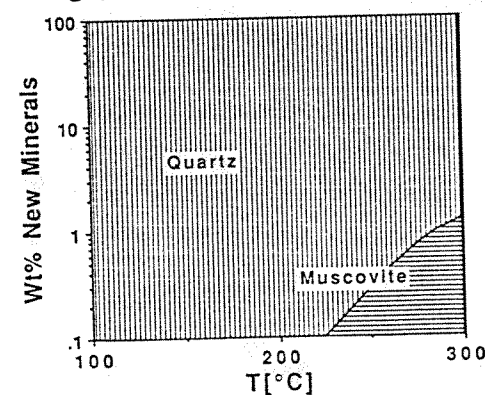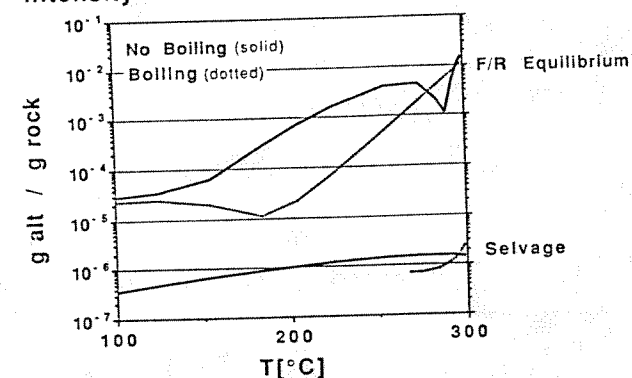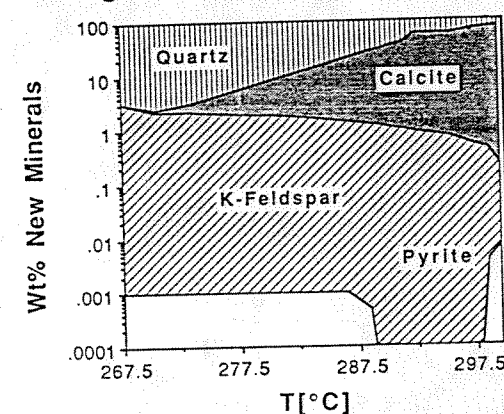
Selvage, No Boiling

FIG. 1. The proportion of hydrothermal minerals precipitated by cooling in a selvaged vein when 1 g of water has passed through every cm³ of rock between isothermal surfaces perpendicular to flow differing in temperature by 1°C.

Selvaged, Boiling

FIG. 3. The proportion of hydrothermal minerals precipitated by cooling and boiling in a selvaged vein. Same conventions as in Figure 1.

A
F/R Equilibrium, No Boiling
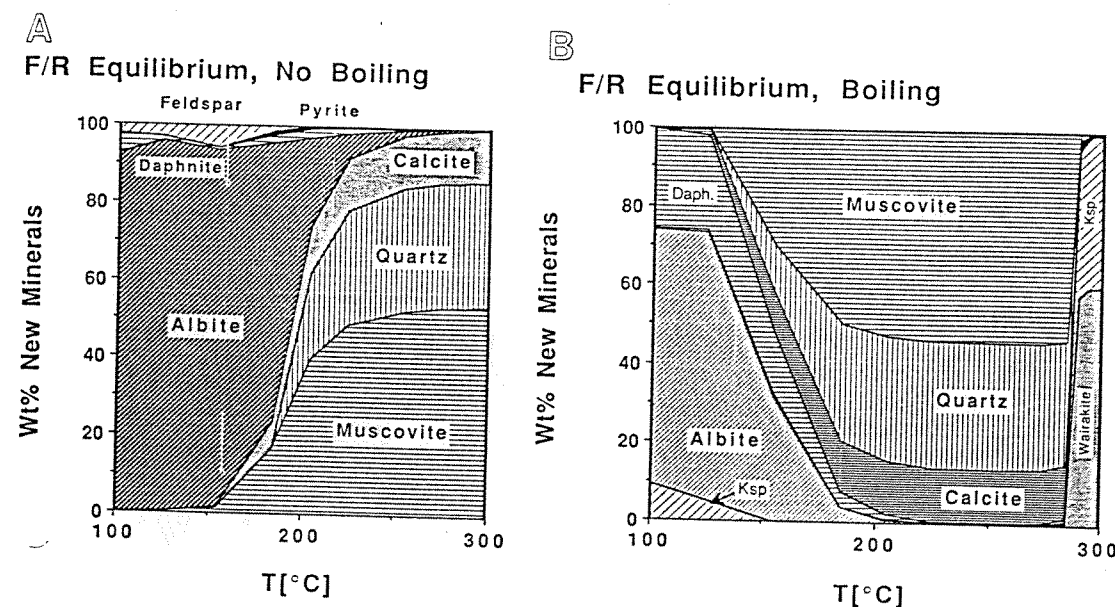
B
F/R Equilibrium, Boiling

FIG. 4. The proportion of hydrothermal minerals precipitated by (A) cooling and by (B) cooling and boiling if chemical equilibrium is maintained with the full set of host-rock buffer minerals. Same conventions as in Figure 1.

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, noting that the pressure gradient in most boiling hydrothermal systems is close to cold-water hydrostatic for reasons discussed by Elders (1966), we can convert the temperature profile in Figure 4b to depth and replot the result in Figure 5. Figure 5 emphasizes the effects of the nonlinear temperature gradient probable in hydrothermal systems, whether

F/R Equilibrium, Boiling

FIG. 5. Replot of Figure 4 with temperature converted to depth on the abscissa assuming a cold water hydrostatic gradient.

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 2, 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 EQ3/6 approach where no mineral in the data base is allowed to be super- or undersaturated. Some (e.g., Giggenbach, 1981, 1988; 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
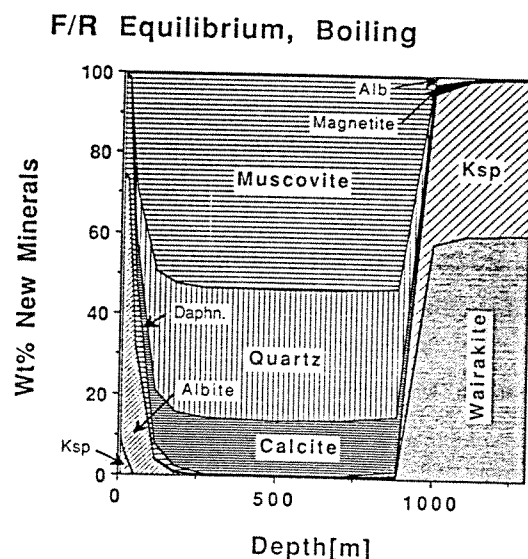
as thermodynamically expected. This freedom has been exercised here with respect to methane, which could have been but was not included as a gas phase, and in the selection of the buffer minerals. Others believe it better to automatically select the most unstable set of buffer minerals. While defending the general approach taken here, it is admitted that the particular buffer chosen 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 overlain by quartz-muscovite alteration is a common association. Gold mineralization is often associated with muscovite, quartz, and calcite. The near-surface albitic 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 for 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 nonselvaged 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 fluids 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 in a vein halo. 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 pertain. 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 pertain. Even then kinetics may not allow rapid enough mineral precip-

itation 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 (1,000×) difference in new mineral formation per unit fluid throughput between the selvaged and nonselvaged (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

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