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How potassium silicate alteration suggests the formation of porphyry ore deposits begins with the nearly explosive but barren expulsion of large volumes of magmatic water

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Abstract

The rate, duration, and volume of reactive aqueous fluids injected into fractured rock are recorded in the pattern of rock alteration. The volume of altered rock records the total mass of fluid expelled. The width of the transition to fresh rock indicates the rate of expulsion, and division yields its duration. We derive mathematical expressions that capture these relationships and are easy to apply, verify them against finite difference simulations, and use them to determine the time required to produce the early and extensive potassium silicate alteration observed in porphyry deposits at Butte, Montana, and Bajo de la Alumbrera, Argentina. The analysis suggests that potassium silicate alteration was produced, and a larger volume of rock heated to near magmatic temperatures, when magma bodies ~1 km (Alumbrera) to ~8 km (pre-main stage Butte) in diameter lost their volatiles in ~20 and ~900 yr, respectively. Metals were deposited as the venting shut down and the potasically-altered system cooled over a much longer period of time. The voluminous, early, and rapid release of large volumes of magmatic volatiles has broad implications for deposit formation, exploration, and the dynamics of magma devolatization. The analysis illustrates the conceptual and scientific utility of simple mathematical expressions that capture both global and local mass balance relationships, and suggests where better parameter definition and additional kinds of modeling could further constrain estimates of the duration of venting.

Keywords: vein halo; alteration of fractured rock; potassium silicate alteration; duration of ore deposition; porphyry deposits; chemical reaction in fractured rock; rate of venting of magmatic volatiles; explosive volcanism; Butte; Alumbrera

1. Introduction

This paper addresses, with a set of simple semi-analytical mass balance equations, the alteration that occurs when a volume of reactive fluid is injected into a fractured rock. Our primary interest is to determine the interval of time over which the fluids have been injected. This is possible because the rate of loss of reactive chemicals flowing through fractures in the rock is controlled by their diffusion into the adjacent host, and therefore the width of the transition zone from fully altered to fresh host is related to the rate of fluid movement through the fractures. The total amount of reactive fluid injected is measured by the total volume of

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altered rock. Division of the total alteration by the rate of alteration gives the duration of alteration.

The equations that we derive involve easily accessible geologic parameters. They can be used to interpret alteration by any "reactive" component in a fluid moving through rock fractures, and thus could potentially be applied to a large number of problems. For example, they could be applied to the loss of reactive contaminants flowing through fractured rock, or to the neutralization of acid mine waters seeping into fractured rock. We confirm their mathematical derivation and illustrate their utility by using them to analyze a finite difference simulation of acid alteration. We then apply the equations to interpret potassium silicate alteration in two porphyry copper systems of very different size. The surprising result is that potassium silicate alteration in these two porphyry systems was probably accomplished in a very short period of time when a large volume of magmatic volatiles was rapidly released, a large volume of host potassically altered, and an even larger volume of host heated to ~600 °C or more. Ore minerals were deposited and other kinds of alteration produced as the system cooled. The initial venting could have been so rapid as to be best described as a barely-controlled explosive volatile eruption. The volume of initially vented volatiles and of volume of intrusion needed to supply them is estimated. This is of interest because drilling sufficient to map a 10 km diameter intrusion up to 10 km below an ore deposit will probably never be feasible, and geophysical techniques cannot easily distinguish those parts of a composite intrusion that devolatized to produce a porphyry deposit from those that did not. As radiometric dating techniques have improved, estimates of the duration of ore deposition has decreased, but radiometric methods are still a long way from being able to constrain events that took place millions of years in the past and lasted less than 1000 yr. Yet the rapidity of magmatic fluid expulsion is important to the physics of how magmas dewater, and therefore quantitative estimates based in geologic observations such the transition from fresh to altered host can be important.

We begin by considering how a reactive fluid passing through a single fracture alters the surrounding rock. We adopt a simple vein halo model in which the reactive component(s) in the fracture diffuse through the water-filled pores of the host to react with minerals in the host. A reaction zone moves outward with time from the vein and leaves behind a zone where the minerals have fully reacted. In geological terminology this "fully reacted" zone is called a vein halo or selvage. We use the term halo here because to us selvage implies that mineral precipitation restricts chemical diffusion into the host (e.g., Cathles, 1991), and this did not occur in the cases we consider. The fracture is called a vein because minerals (such as quartz or sulfides) are usually precipitated in it. In porphyry deposits the vein widths are usually <2 cm, and might more properly be called veinlets (Seedorff et al., 2005). The importance of the halo around the fracture or vein is that it indicates that the rate of loss of reactive components from the fracture is controlled by diffusion, which is a basis of our analysis in this paper.

Fig. 1. Image of a typical pyrite vein with a grey sericite (acid) alteration halo and an outer fringe of biotite alteration. This illustrates how one style of alteration can be superimposed on an earlier one and provides a visual depiction of what we mean by vein and vein halo. The picture was provided by Brian Rusk.

Once we have derived mass balance equations that describe how reactive components are lost from a single fracture and how the concentration of reactive components change with distance along the fracture, we add more fractures and define a zone of pervasive alteration near the source where the halos meld (just overlap) and the host is fully reacted. We then conceptually generalize the halo taper outward from this zone and consider it, equivalently, as a transition from fully altered to fresh host. The width of the transition zone and the radius of pervasive alteration are the key observational parameters in our model.

Vein halos have been used by geologists and engineers to understand and model the rates of chemical

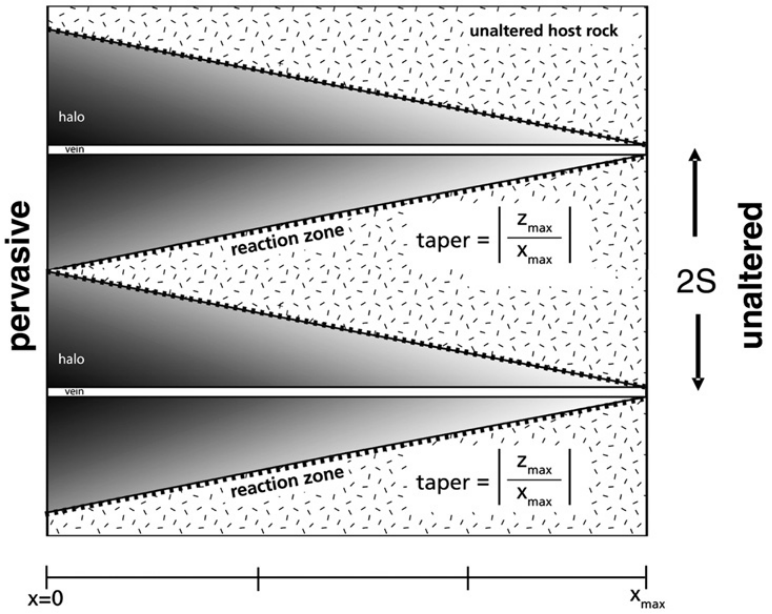

Fig. 2. Alteration halos around two parallel fractures (veins) at a time when the halos have just merged where the reactive fluid enters the fractures at $x=0$. Chemical reaction between a reactive chemical and specific minerals in the host rock occurs in a thin reaction zone, and the halo grows as this zone moves outward with time. No chemical reactions occur in the halo.

reactions for decades. The chemical engineering literature calls diffusional halo models shrinking core models (e.g. Levenspiel, 1967). Their concepts have been successfully adapted to describe the leaching of sulfide blebs from rock fragments in industrial leach dumps where centimeter-wide halos leached of disseminated sulfide blebs develop in ~30 yr (Cathles and Apps, 1975; Cathles, 1979). Diffusion from fractures has been used to constrain the duration of mineralizing events in very different ore-forming systems than we consider here (e.g., Lavery and Barnes, 1971). Theoretical discussion of vein halo formation has been offered by Steefel and Lichtner (1998a,b). Vein halos were described at Butte by Meyer et al. (1968) and Sales and Meyer (1949). Previous modeling of acid (sericite) alteration halos at Butte (Fig. 1) by Geiger et al. (2002) determined that each halo took about 20 yr to form. Our chemically less rigorous approach differs from theirs in considering vein halos in a simpler fashion and in relating them, in a system-wide fashion, to the width of the transition zone from altered to fresh rock and thereby to the rate of fluid expulsion. We also apply our analysis to potassium silicate alteration halos whereas they considered sericite acid alteration halos at Butte.

2. Theory

The rate of formation of an alteration halo surrounding a rock fracture through which aqueous fluid is flowing is governed by the rate of diffusion of the chemical component (which we call here the critical component) that diffuses most slowly from the fracture through the halo to unaltered rock at its edge. Within the halo, fluid does not react with the rock because the reactive minerals in the halo have been removed by dissolution or conversion to stable minerals. Reaction occurs only in a narrow zone very near the edge of the halo, as illustrated in Fig. 2. The thickness of the reaction zone decreases as the reaction kinetics increase (Cathles and Apps, 1975). Beyond this zone the pore fluid is in equilibrium with the host rock.

The total concentration of the critical component in the vein is not necessarily the concentration that drives diffusion for two reasons. First, since the total concentration of a species is comprised of a number of subspecies (for example the total concentration of K might consist of K^+, KCl, KOH, etc.) it is the concentration of the most abundant of the sub-species that counts, and this is some fraction of the total concentration. Second the total concentration of the critical species at the edge of the halo is not necessarily zero; it is the concentration that is in chemical equilibrium with the unaltered host rock. The difference between the vein and equilibrium concentrations can be much smaller than the vein concentration. In our model we take both of these factors into account by assuming that the concentration drop across the halo is some fraction, f, of C in the vein. We write the total concentration of C in the vein as $C_{\sum C_i}$

Table 1
Glossary of parameters

Parameter	Definition	Value/units	Comment or reference
$C^o_{\sum C_i}$	Concentration of reactable component C in the magmatic source fluid	**0.3** wt.% K	Butte
		10 wt.% K	Alumbrera
$C_{\sum C_i}$	Concentration of reactable component C in vein some distance from the source	$\leq C^o_{\sum C_i}$	calculated in the finite difference simulations
D	Diffusivity of critical species in water	**1.19** m^2/yr	Increased from 400 °C value from Geiger et al. using Arrhenius equation with activation energy of 5 kcal/mole K
D_E	Effective diffusion constant for critical species through host	$=\frac{\phi f D}{\tau}$	
f	Fraction of total hydrogen concentration in magmatic source fluid which drives diffusion	0.6	FD confirmation calculations
		0.3	Butte and Alumbrera
f_{active}	Fraction of veins open at any one time	1	FD confirmation calculations
		0.1 < **0.3** < 1	Butte and Alumbrera
ϕ	Host rock porosity	0.01	FD confirmation calculations
		0.001 < **0.005** < 0.01	Butte and Alumbrera
X_{H2O}	Mass fraction of volatiles (fluids) in intrusion	**0.05**	Hornblende stability in felsic magma
G	Component added/removed to fully alter host	**1** wt.% K	Butte
		2 wt.% K	Alumbrera
$\bar{G}$	m^3 Magmatic fluid required to alter m^3 host	$=\frac{\rho_r G}{\rho_f C_{\Sigma C_i}}$	
H	Length of the cylinder alteration axis	**7000** m	Butte
		1200 m	Alumbrera
j_c	Diffusional flux rate of component C across alteration halo	mol m^{-2} s^{-1}	Eq. (1)
J_c	Diffusional flux of component C across halo from t=0 to t	mol m^{-2}	Eq. (2)
Δr	Width of transition from unaltered to altered host	~**230** m	Butte
		~**75** m	Alumbrera
		125 m	FD confirmation calculations
r_{perv}	The radial distance pervasive alteration extends form a magmatic fluid source	**1200** m	Butte
		150 m	Alumbrera
		1500 m	FD confirmation calculations
r_{intr}	Radius of spherical intrusion needed to supply volatiles required to produce potassium silicate alteration	m	
ρ_f	Density of magmatic fluid	**400** kg/m^3	Appropriate for 600 °C magmatic fluids at Butte
ρ_r	Density of host rock	**2712** kg/m^3	Geiger et al. (2002)
S	Half the spacing between veins; effective spacing	0.0235 m	FD confirmation calculations
		0.008 < **0.023** < 0.05 m	Butte (and Alumbrera)
T	Temperature of potassic alteraton	600 °C	Estimated at Butte by Brimhall (1977)
taper	Slope of alteration halo around vein	(−)	
t_{meld}	Time required for halos from adjacent vein/fractures to meld	yr	Eq. (10)
t_{venting}	Total duration of magmatic fluid venting inferred from halo formation	yr	Eqs. (4), (11), (14a,b)
τ	Parameter that accounts for impact of pore tortuosity and pore constrictions on diffusion	19 < **30** < 100	$=\frac{0.68}{\phi^{0.72}}$ Geiger et al. (2002)
$\dot{V}$	The volume flux of magmatic source fluid through one vein	m^3/m/yr	
$\dot{V}_{r_{\text{perv}}}$	The volume flux of magmatic source fluid through one vein at r_{perv}	m^3/m/yr	
V_{fluid}	Volume of magmatic fluid required to produce the total observed volume of potassium silicate alteration	$=\bar{G}V_{\text{alt}}$	

(continued on next page)

Table 1 (*continued*)

Parameter	Definition	Value/units	Comment or reference
V_{alt}	Volume of potassium silicate alteration	m^3	Observed
V_{intr}	Volume of magma required to supply volatiles	m^3	
v_H	Velocity at which vein halos extend from source	m/yr	Eq. (8)
v_{perv}	Velocity of outward progression of pervasive alteration	m/yr	Eq. (9)
x	Distance along vein	m	
x_{max}	Maximum distance from source to which host has been altered	m	
z	Width of alteration halo measured normal to vein	m	

to emphasize that the total concentration is comprised of the sum of the concentrations of the aqueous species that contain C. The flux of C across the halo is then:

$$j_c = -\frac{D\phi\rho_f}{\tau}\cdot\frac{fC_{\sum C_i}}{z}, \tag{1}$$

where j_c is the moles per m^2-second of C diffused across the halo, z is the width of the halo, D is the diffusion constant of the components that contain C in water at temperature, ϕ is the vein halo porosity, τ is a factor that takes into account the effects on diffusion of pore tortuosity and constrictions, and ρ_f the density of the fluid filling the pores. All parameters are defined in Table 1.

Over the time t that is required for the halo to grow to width z, the cumulative flux of C from a unit area of the vein surface is:

$$J_c = 2\cdot\frac{D\phi\rho_f}{\tau}\cdot\frac{fC_{\sum C_i}}{z}\cdot t. \tag{2}$$

Here J_C is the flux of C in moles per m^2. It equals t times the average flux from time zero to time t. The average flux over t is approximated as twice the flux at t, which accounts well for the faster diffusion at early times when the halo width z is small.

The vein halo width at time t is determined by mass balance. This requires that the cumulative loss of the critical component from the vein equal that in the pores of the vein halo plus that consumed by reaction in the rock. If G is the moles of the critical component per kilogram rock consumed in converting fresh host to halo, and ρ_r is the density of the host rock, the moles of critical component consumed per m^2 surface of the vein is $\rho_r\, G\, z$. The critical component in the pores of the halo is $\frac{1}{2}z\phi\rho_f C_{\sum c_i}$. Setting Eq. (2) equal to the sum of these terms and rearranging yields:

$$z(t) = 2\sqrt{\frac{f\,Dt/\tau}{1+\left(\frac{2G\rho_r}{\phi\rho_f C_{\sum c_i}}\right)}} = 2\sqrt{\frac{D_E t}{\phi + 2\,\bar{G}}}\ . \tag{3a}$$

In the term to the right of the second equals sign we have defined $\bar{G}\equiv\frac{\rho_r G}{\rho_f C_{\Sigma C_c}}$ and $D_E\equiv\frac{\phi f D}{\tau}$. $\bar{G}$ is a dimensionless parameter that equals the volume (m^3) of fluid required to alter a m^3 of rock. D_E is the effective diffusion constant for the rock. Note that if $G=0$ this expression reduces to a form similar to the familiar thermal diffusion equation where fD/τ corresponds to thermal diffusivity. The expression can be simplified if $\phi << 2\bar{G}$:

$$z(t) = 2\sqrt{\frac{D_E t}{2\,\bar{G}}}. \tag{3b}$$

The duration of venting is measured by the halo width at the source, which we assume is located at $x=0$:

$$t_{\text{venting}} = \frac{z_{x=0}^2\,\bar{G}}{2D_E}. \tag{4}$$

The distance, x_{max}, from the source to the outer limit of alteration increases as a function of the venting rate and time. Finite difference simulations discussed below show that the width of the halo decreases linearly with distance from the source. If this is the case, the moles of C reacted per unit length of vein perpendicular to flow between $x=0$ and x_{max} is $\rho_r\, Z_{x=0}\, G\, x_{max}$. Here we have considered the losses from both sides of the vein. This loss must equal the moles of C delivered over the duration of venting, $\dot{V}C_{\sum c_i}t_{\text{venting}}$, where $\dot{V}$ is the volume flux of fluid per meter length of vein perpendicular to flow, so:

$$x_{\max} = \frac{\rho_f\dot{V}C_{\sum C_i}t}{\rho_r G z_{x=0}} = \frac{\dot{V}t}{\bar{G}z_{x=0}}. \tag{5}$$

The halo taper is determined by Eqs. (3b) and (5):

$$\text{taper} = \frac{z_{x=0}}{x_{\max}} = \frac{\bar{G}z_{x=0}^2}{\dot{V}} = \frac{2D_E}{\dot{V}} = const. \tag{6}$$

The taper is a constant for a constant flow rate through the fracture because both $z_{x=0}$ and x_{max} are proportional

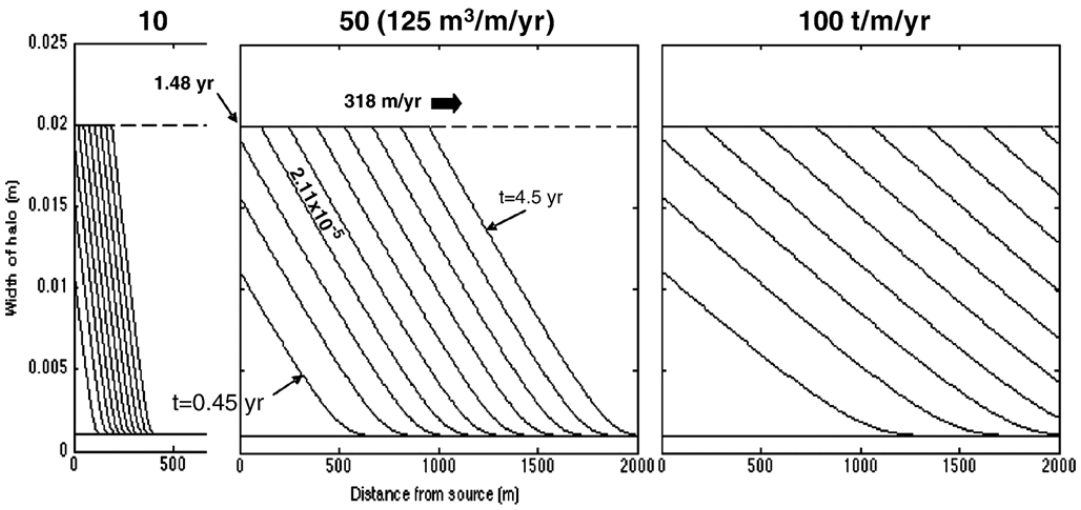

Fig. 3. Numerical simulation of alteration around a fracture (vein) in which reactive fluid is flowing at 10, 50 and 100 tonnes/yr/m of vein length perpendicular. Lines indicate the margin of the halo (abrupt transition from fully altered to fresh rock) at 0.45 yr intervals. The vein spacing is assumed to be 4 cm, and the halos thus merge when the halo around a single vein is 2 cm wide. In the central figure the halos merge at 1.48 yr, the taper (slope) of the halo is 2.11×10^{-5} at all times, and the zone of pervasive alteration moves to the right at 318 m/yr. As discussed in the text, these values can be calculated using the semi-analytic expressions derived in the text. The parameter values used in this particular simulation are given in Table 2.

to $\bar{G}^{-1}$ and grow at a rate proportional to $\sqrt{t}$. It follows from Eq. (6) that:

$$x_{\max} = \frac{z_{x=0}}{\text{taper}} = \frac{\dot{V} z_{x=0}}{2D_E}. \tag{7}$$

Thus the maximum distance veins with halos extend from the source measures the flux, $\dot{V}$, of aqueous fluids through the vein.

At constant venting rate, the rate at which vein halos extend from the source, v_H, is inversely proportional to the square root of time, as can be seen from taking the derivative of Eq. (7):

$$v_H = \frac{\partial x_{\max}}{\partial t} = \frac{\dot{V}}{2D_E}\sqrt{\frac{D_E}{2\bar{G}t}} = \frac{\dot{V}}{2z_{x=0}\bar{G}}. \tag{8}$$

So far we have considered halo formation around a single, isolated fracture (vein). Rock fractures generally have a roughly constant spacing, and at some point in time the halos from adjacent fractures will meet, and the assumption of isolated fractures will no longer be valid. If the fracture spacing is $2S$, the halos from adjacent fractures will meet or meld when $z_{x=0}=S$, and from this time onward the source fluid will move, at least for a time, through fully altered rock. The width of the pervasively altered zone will increase at a rate v_{perv}:

$$v_{\text{perv}} = \frac{\dot{V}}{2\bar{G}S}. \tag{9}$$

From Eq. (3b), the time for the halos to meld at $x=0$ is:

$$t_{\text{meld}} = \frac{S^2\bar{G}}{2D_E}. \tag{10}$$

The duration of venting is the time for the halos to meld at the source plus the time required to form the pervasive alteration:

$$t_{\text{venting}} = t_{\text{meld}} + \frac{x_{\text{perv}}}{v_{\text{perv}}}. \tag{11}$$

From Eq. (7) with $z_{x=0}=S$ so that $x_{\max}=\Delta x$ (the distance alteration extends from the edge of pervasive alteration) and (9), and (10) it can be seen that if the extent of pervasive alteration from the source is large compared to the distance alteration persists beyond the edge of the pervasive alteration, the second term in Eq. (11) dominates and alone provides a reasonable estimate of the duration of venting.

In summary, the model described above shows that the duration of venting can be inferred from vein halo width (3b), or by dividing the extent of pervasive alteration by the venting rate (11). The venting rate can be inferred from the halo taper (6) which is the same as half the fracture spacing divided by the width of the transition zone separating pervasively altered and fresh rock.

In nature, a reactive fluid usually moves radially, not linearly from its source, so for application we need to assess how these concepts are affected by radial flow. If the volume of alteration is mainly that associated with

Table 2
Venting times and other characteristics calculated from equations in test

Parameter	FD Calculations	Butte	Alumbrera
$\bar{G} = \frac{\rho_r G}{\rho_f C_{\Sigma C_i}}$	10.58	**22.6**	**1.35**
$D_E = \frac{\phi f D}{\tau}$	1.428×10^{-3} m^2/yr	**5.25×10^{-5}** m^2/yr	**5.25×10^{-5}** m^2/yr
taper	2.11×10^{-5} (Fig. 3) 2.18×10^{-5} (Eq. (6))		
t_{meld}	1.48 yrs (Fig. 3) 1.48 yrs (Eq. (10))		
v_{perv}	318 m/yr (Fig. 3) 295 m/yr (Eq. (9))		
$V_{fluid} = \bar{G}V_{alt}$		10^{11} m^3	10^8 m^3
r_{intr}		8.3 km	0.86 km
$t_{venting}$	13 yrs in simulation (Fig. 4) 8.2 yrs Eq. (14b)	281<**888**<44,200 yrs (Eq. (14a))	6.3<**20**<996 yrs (Eq. (14a))

The bold (base case) parameter values are used for the Butte and Alumbrera porphyry systems.

the pervasive alteration, the total fluid volume required to produce the alteration is:

$$V_{\underset{cyl}{fluid}} = \bar{G}V_{\underset{cyl}{alt}} = \pi r_{perv}^2 H\bar{G} \tag{12a}$$

$$V_{\underset{sph}{fluid}} = \bar{G}V_{\underset{sph}{alt}} = \frac{4}{3}\pi r_{perv}^3\bar{G}, \tag{12b}$$

where r_{perv} is the radius of pervasive alteration, H is the vertical extent of a line source, V_{fluid} is the total volume (m^3) of reactive fluid expelled from the source, and the subscripts cyl and sph refer to cylindrical or spherical flow.

If veins with alteration halos extend a distance away from the pervasive alteration that is short compared to the radius of the pervasive alteration, the flow rate will be approximately constant over the interval of transition to fresh rock, and, assuming constant fracture separation, the increase in the number of veins over this distance will be small. Approximately, the halo taper will be the same as in the linear case (Eq. (6) and Fig. 2), and:

$$\text{taper} = \frac{2D_E}{\dot{V}_{r_{perv}}} = \frac{S}{\Delta r}, \tag{13}$$

where Δr is the distance veins with halos extend from the edge of the pervasive alteration at r_{perv}, and $\dot{V}_{r_{perv}}$ is the flow rate through the veins at a distance r_{perv} from the source. Stated another way, the transition distance, Δr, in the spherical case is taken to be the equivalent of x_{max} in Fig. 2, where the origin $x=0$ is now the edge of the spherical or cylindrical pervasive alteration. The duration of venting is the total volume of fluid expelled to alter the rock as observed divided by the total fluid expulsion rate which equals the flow rate through the veins times the length of vein per m^2 ($=1/S$) times the enclosing area:

$$t_{\underset{cyl}{venting}} = \frac{V_{fluid}S}{2\pi r_{perv}H\dot{V}_{r_{perv}}} = \frac{V_{fluid}S^2}{4\pi r_{perv}HD_E\Delta r f_{active}} = \frac{1}{4}\frac{\bar{G}S^2 r_{perv}}{D_E\Delta r f_{active}}, \tag{14a}$$

$$t_{\underset{sph}{venting}} = \frac{V_{fluid}S}{4\pi r_{perv}^2\dot{V}_{r_{perv}}} = \frac{V_{fluid}S^2}{8\pi r_{perv}^2D_E\Delta r f_{active}} = \frac{1}{6}\frac{\bar{G}S^2 r_{perv}}{D_E\Delta r f_{active}}, \tag{14b}$$

If the fraction of veins open at any time in the transition zone is f_{active}, the flow rate in each active vein would be increased as if Δr equaled $V_r f_{active}$. Thus the time required for alteration will be increased by $1/f_{active}$. We have inserted this factor in the above expressions.

The average rate of venting is $V_{fluid}/t_{venting}$. Since the volume of altered host is V_{alt} and $V_{fluid}=\bar{G}V_{alt}$ (Eq. (12a,b)), the mass fraction of volatiles in an intrusion is X_{H2O}, the minimum volume of the intrusion needed to supply the magmatic volatiles is:

$$V_{intr} = \frac{\bar{G}V_{alt}}{X_{H2O}\frac{\rho_r}{\rho_f}}. \tag{15}$$

3. Finite difference confirmation

The semi-analytic model described above contains potentially useful concepts in a form that is very easy to apply. To gain confidence in the model and verify some of its key assumptions, especially the linear halo taper, a

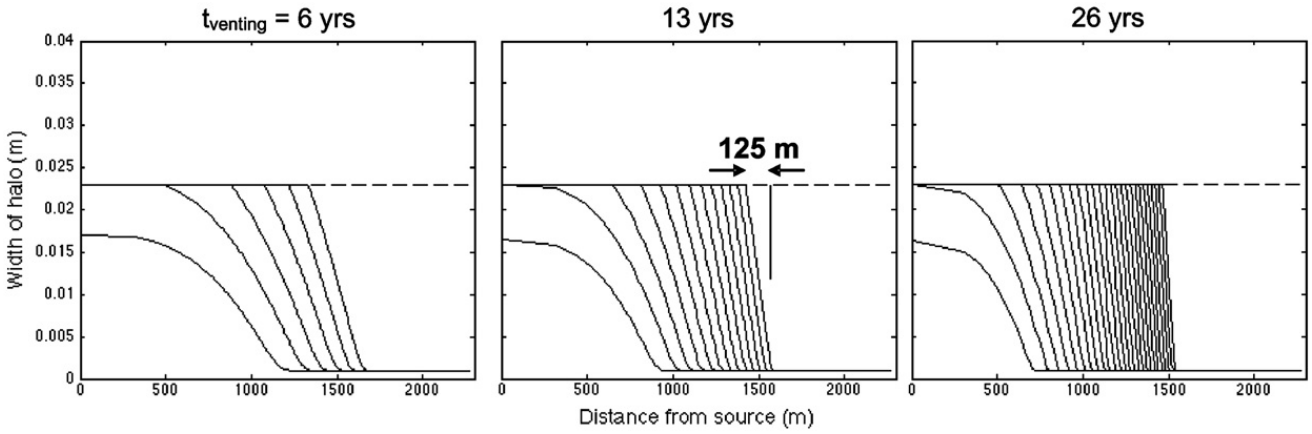

Fig. 4. Numerical simulation of alteration caused by spherically-symmetric fluid flow from a point source through veins separated by ~4 cm. The volume of fluid numerically injected was such as to produce alteration to a distance of 1500 m from the source in all cases. This volume was injected over 6, 13, and 26 yr respectively in the three panels shown above. The transition from fully altered to unaltered occurs over ~125 m for the case shown in the middle panel. The duration of venting suggested by Eq. (14b) for 1500 m of pervasive alteration and a transition zone 125 m wide is 8.4 yr which compares favorably with the numerical injection duration of 13 yr.

finite difference model of vein halo development was constructed. Here we discuss that model, show that it confirms our derivation of the semi-analytic model presented above (including the linearity of taper), and show how the semi-analytic model can be used to quickly interpret the numerical alteration produced by spherical venting from a point source in a finite difference calculation. We then apply the semi-analytic equations to analyze potassic alteration in two porphyry copper systems, and discuss some of the implications of these applications.

The finite difference model assumes that away from the vein, the alteration halo grows by diffusion as a function of the square root of time according to Eq. (4). Distance along the numerical vein is divided into cells of length l, where l equals the distance the fluid travels in one timestep. To avoid infinite diffusion rates, each cell is given a very thin halo at the start of the simulation. At time 0, fluid with initial $C^o_{\sum C_i}$ is introduced into the first cell. Diffusion is calculated perpendicular to the vein for the specified timestep assuming a linear gradient to zero across the width of the halo. The moles of C diffused from the vein over the timestep (typically 3×10^{-4} yr) is computed using Eq. (1). At the end the timestep, the halo width in the first cell is increased in accordance with the amount of C diffused out of the vein over the timestep. The $C_{\sum C_i}$ concentration in the vein is decreased by the amount needed to balance this loss, and this fluid is moved to the next downstream cell, where the process is repeated and the remaining $C_{\sum C_i}$ is passed on to the next downstream cell, etc. Vein fluid in the first cell is always replaced with source fluid of concentration $C^o_{\sum C_i}$. A simulation typically involves $\sim10^5$ timesteps. The finite difference model was constructed in MatLAB. Further details are given in Shannon (2006).

Finite difference simulations of halo development are show for a set of parallel veins separated by $2S$ and three different flow rates through the veins in Fig. 3. The taper of the halo is linear in all cases. Table 2 gives the parameter values used in the finite difference simulation and shows that the values of taper, time for the halos to meld, and the rate at which the pervasively altered zone moves outward from $x=0$ are predicted with <10% error by Eqs. (6), (9), and (10).

To account for radial flow, the numerical methods described above were converted into a spherical model by replacing the cells of equal length with shells of equal volume. As before, the fluid was moved from one shell to the next in each timestep, and the width of each shell was such that the fluid traversed every shell at each timestep. If vein spacing is constant and all veins contain equal volumes of fluid per unit area of vein, the radius of the outer boundary of each shell is $r_o\sqrt[3]{n}$, where is n is the number of the shell ($n=1$ represents the innermost sphere surrounding the source, $n=2$ represents the first shell, etc). For example, if the radius of the innermost ($n=1$) sphere is r_o, the width of the first shell enclosing it is $\Delta r=0.26\ r_o$, and the width of the 10th shell is $r_o\left(\sqrt[3]{10}-\sqrt[3]{9}\right)=0.074\mathrm{r_o}$. Radial distance is collapsed because the fluid velocity drops with radial distance in radial flow, but the modeling is otherwise identical to the linear flow case. We just transform (collapse) the distance axis to obtain the spherical solution.

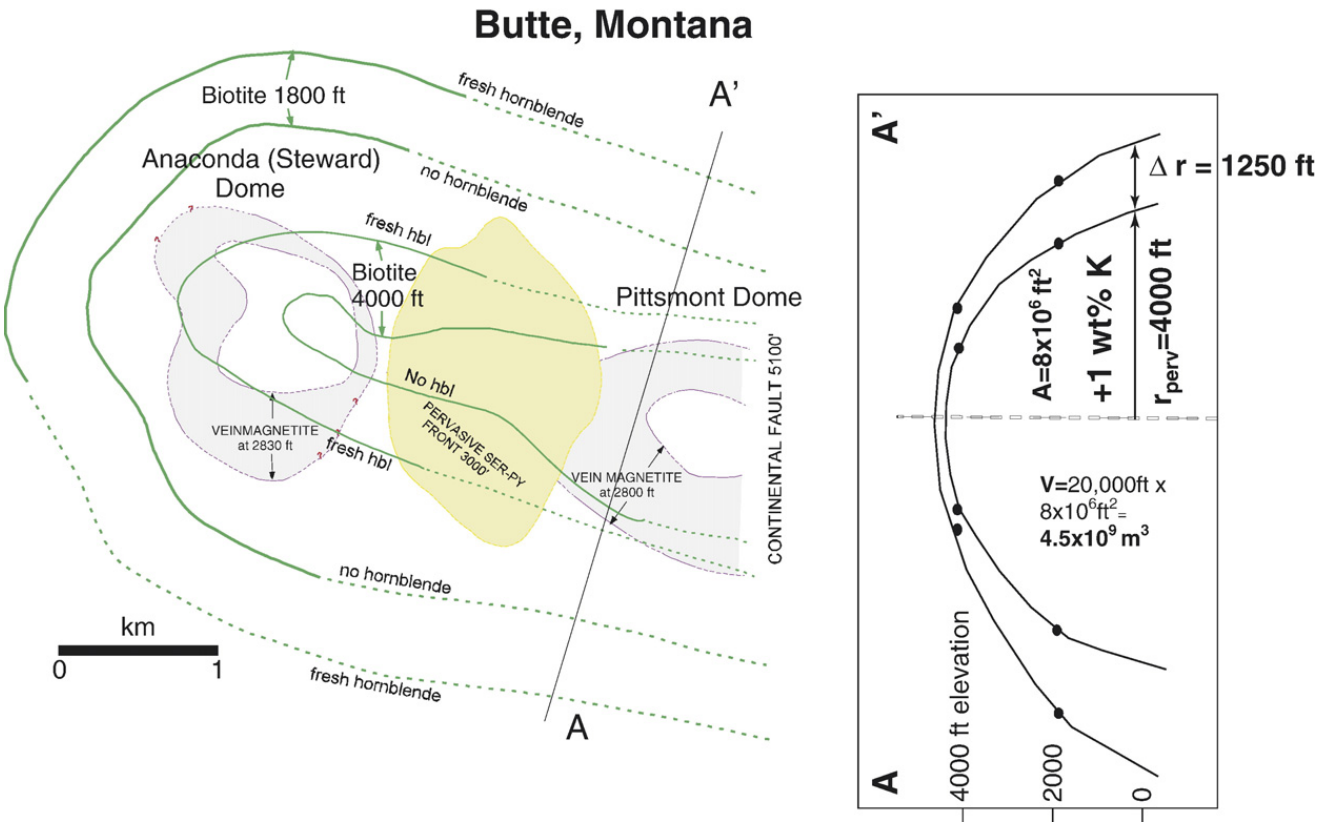

Fig. 5. (a) Plan map of potassic alteration at Butte after Roberts (1975). Contours show the outer (fresh hornblende) and inner (no hornblende) edge of the potassium silicate (biotite) alteration at 1800 and 4000 ft elevation. Areas at ~2800 ft elevation with vein magnetite are shaded. These correspond with Mo enrichment and mark the location of the Anaconda and Pittsmont Dome centers of porphyry mineralization. The Continental fault which offsets the potassium silicate alteration marks the left edge of the diagram. (b) A cross section of the alteration along section A–A′. As discussed in the text, within the pervasive zone the potassium content of the Butte Quartz Monzonite is increased by about ~1 wt.%. The potassium silicate alteration extends about 8000 ft to the right (on the other side of the Continental fault). Including this, the potassium silicate alteration has a total length of about 20,000 ft (7 km). If the pervasively altered volume is approximated as a half cylinder lying on its side, the altered volume is $\sim 4.5 \times 10^9$ m^3. The potassium silicate alteration is much more extensive than the minearalization and other kinds of alteration. Their extent is indicated by the distribution of vein magnetite and pervasive sericite–pyrite alteration. This figure is a simplified version of a diagram prepared by Mark Reed (1979, Anaconda Report, unpublished) based on mapping by Steve Roberts (1975), with additions by John Dilles.

Fig. 4 shows how halos form around veins when the flow is spherically symmetric and directed outward from a point source. Table 2 compares the estimated duration of venting calculated from Eq. (14b) to the duration of venting in the finite difference simulation in Fig. 4. Taken together, Figs. 3 and 4 and Table 2 verify the utility of the semi-analytic equations derived in the previous section, and illustrate how the radius of pervasive alteration and the width of the transition from fully altered to unaltered host can be used to estimate the time interval over which reactive fluid has been propelled through a host rock. The duration of venting estimated by Eq. (14b) for the spherical venting case is about 40% low (8.2 vs. 13 yr). This discrepancy is greater than that between the numerical and semi-analytic equation estimates of the taper, rate of migration of pervasive alteration, and the time to meld in the linear case, perhaps because we have ignored the drop in fluid velocity across each shell in the numerical model. Correcting this could shrink the transition width in the numerical model and improve the venting duration estimated by the semi-analytic equation. The venting duration estimated by Eq. (14b) is, however, fully accurate enough for our purposes in this paper, and we do not pursue the origin of discrepancies further here.

4. Application to potassic alteration in two porphyry systems

The 76 Ma Butte Quartz Monzonite (BQM) in Montana (Aleinikoff et al., 2000) hosts the Butte porphyry copper deposit, one of the largest deposits of its type in the world. Between 62.5 and 66.4 Ma (Dilles et al., 2003) minerals were deposited from fluids that were expelled from magmas that intruded the BQM below the site of ore

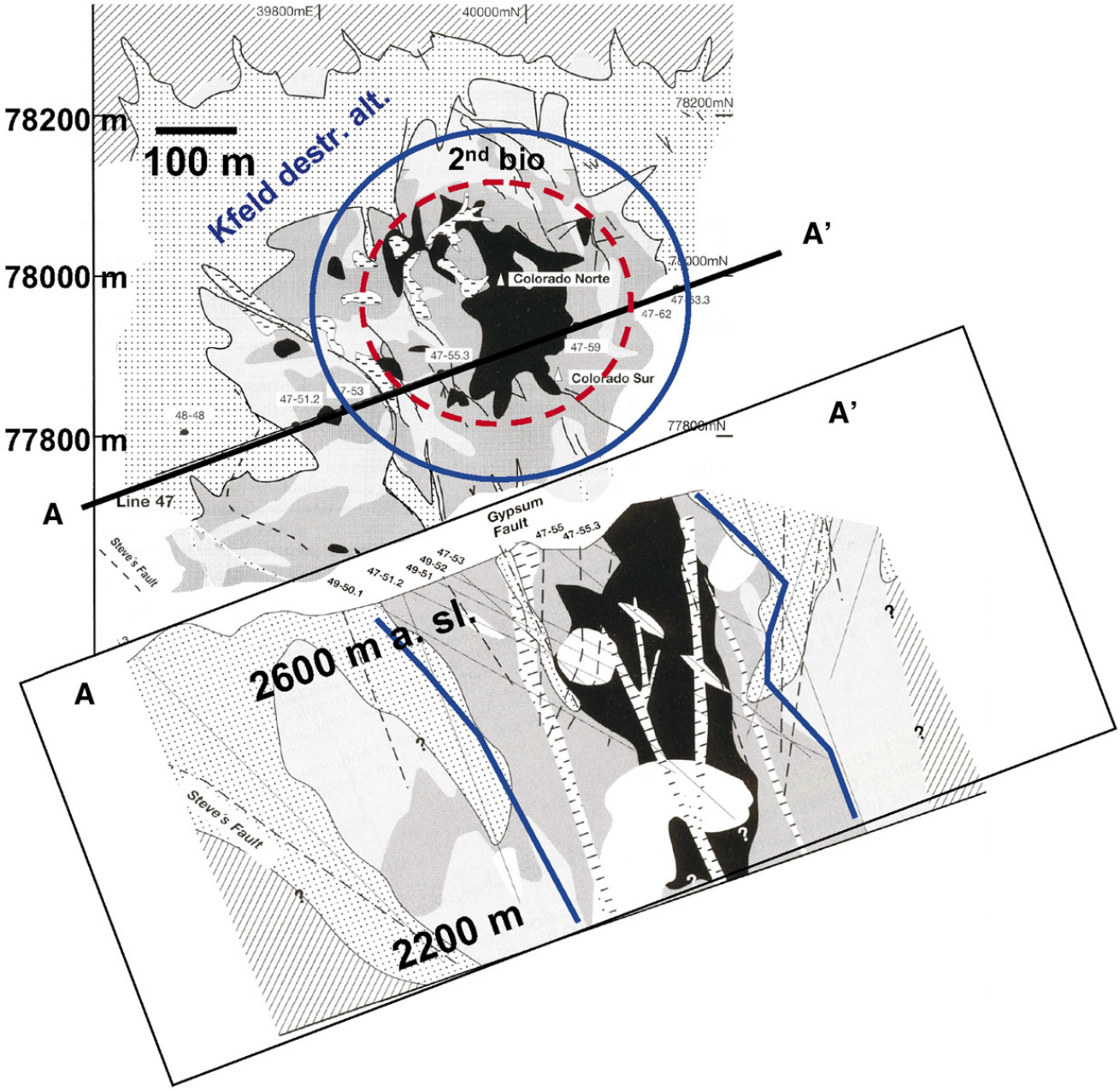

Fig. 6. Composite of figures from Ulrich and Heinrich (2002a,b) showing in plan (top) and section (bottom) the distribution of potassic alteration in the Bajo de la Alumbrera porphyry Cu–Au deposit in Argentina. Black indicates strong K-feldspar alteration with partly intense quartz–magnetite, dark grey moderate to weak K-feldspar alteration with minor magnetite, and light grey the presence of secondary biotite. In the surrounding stippled areas K-feldspar is destroyed by late alteration. As in Fig. 5, the solid lines indicate the approximate outer edge of potassic alteration, and the dashed circle the outer limit of intense (pervasive) K-feldspar alteration. The annulus between the solid and dashed circles is ~75 m and the radius of the pervasive alteration (red dashed circle) is ~150 m. If the pervasive alteration originally extended vertically across 1200 m (3 times that in the section), the volume of pervasive alteration was 8.5×10^7 m^3.

deposition. These fluids initially radiated from a roughly linear vent zone that was approximately 7 km long. The first alteration produced by the "magmatic" volatiles converted hornblende in the BQM to biotite, quartz and anhydrite at temperatures (>600 °C) very close to the intrusion solidus (Roberts, 1975; Brimhall, 1977; Field et al., 2005). The other minerals in the BQM were not affected. The plagioclase and K-feldspar are the same as in the fresh BQM, for example (Brimhall, 1977; Titley, 1982; M. Reed, pc, 2006). The reaction involved (Brimhall, 1985) was:

$$\text{hornblende} + K_2SO_4(aq) + H_2SO_4(aq) \rightarrow \text{biotite} + \text{anhydrite} + \text{quartz}.$$

According to this equation, the addition of K^+ and H^+ from the magmatic fluid converts hornblende to biotite, anhydrite, and quartz. Laboratory experiments have been carried out that elucidate the nature of this rapid reaction (Brimhall, 1985).

The pattern of early potassic alteration at Butte is geometrically very regular, as shown in Fig. 5. There is a central zone along the axis of later mineralization within which the hornblende is completely converted to biotite, and an outer zone in which none of the hornblende is converted to biotite. The alteration morphology is approximately that of the upper half of a cylinder lying on its side. The radius of an inner cylinder, where 100% of the hornblende is destroyed, is ~1220 m, and the width of the transition to an outer cylinder beyond which hornblende is unaltered (100% present) is ~230 m. The increase in potassium in the BQM associated with the conversion of hornblende to biotite is ~1 wt.%. For example biotite contains 8 to 9 wt.% potassium and hornblende 0.8 to 1 wt.%, the Butte Quartz Monzonite contains 12–13 vol.% hornblende and this converts to ~10 vol.% biotite, so there is an increase of ~8 wt.% potassium in ~10 to 12 wt.% of the rock for an increase of ~1 wt.% potassium (modal analyses in Brimhall, 1977; Dilles, pc, 2007). The magmatic fluid contained ~0.3 wt.% potassium (Rusk et al., 2004). Thus about 22.6 m^3 of magmatic water is required to potassically alter 1 m^3 of BQM. Substituting the mid-range (bold) parameters listed in Table 1 into Eq. (14a) indicates that the early potassium silicate alteration was accomplished in about 900 yr (Table 2). In all about 4.5×10^9 m^3 of BQM was altered by ~100×10^9 m^3 of magmatic fluid. If these volatiles were supplied by the expulsion of 5 wt.% water from a magma, the magma volume required is 300×10^9 m^3, which is the volume of a sphere 8.3 km in diameter.

Fig. 6 shows the pattern of potassium silicate alteration in the much smaller Alumbrera porphyry system in Argentina. This deposit has been extensively studied by Ulrich and Heinrich (2002a,b) and Proffett (2003). The zone of potassium silicate alteration is enriched by 2 wt.% potassium, the 50–60 wt.% NaCl magmatic bines responsible for the alteration carried ~10 wt.% potassium, and the radius of pervasive alteration and the width of the transition to unaltered host suggest that the potassium silicate alteration was accomplished in ~20 yr (Tables 1 and 2).

Fig. 7 shows how the volume of the early potassium silicate alteration at Butte and Alumbrera are related to the volume of magma required to supply the magmatic volatiles that produced it. The size of magma intusion needed to supply the volatiles at Alumbrera is much smaller than at Butte, and, because the K content of the magmatic fluid is much greater, the volume of the intrusion at Alumbrera is smaller relative to the volume of potassic alteration there. The porphyry deposit formed from a saline brine. We assume in the magma volume calculation that the magmatic volatiles expelled were these same brines. This is possible if the chlorine content of the magma was high. If, however, the mineralizing brine is a vapor condensate, e.g., if the magma expelled a much larger mass of low salinity fluid which subsequently partly condensed to brine, the volume of the intrusion needed to provide the larger volume of low salinity fluid would of course be larger. Assuming the brine represents a 10 wt.% condensation, the radius of the magma body would be about doubled ($\sim\sqrt[3]{10}$), for example.

5. Parameters used

The duration of venting required to produce the potassium silicate alteration at Butte and Alumbrera is short, but depends on the parameter values listed in Table 1. The values of many of these parameters are uncertain, and where this is the case a range of values is given in Table 1. The bold (mid-range) values in Table 1 are used in the venting duration calculations discussed above and reported in Table 2. Here we discuss how the parameter ranges of the most uncertain parameters ϕ, Δr, S, and f_{active} are assigned. Where the origin of the parameter value is not obvious, we also discuss how we assigned a single (relatively certain) value.

For example, we have taken $f=0.3$ in the Butte and Alumbrera calculations. Giggenbach (1984) has shown

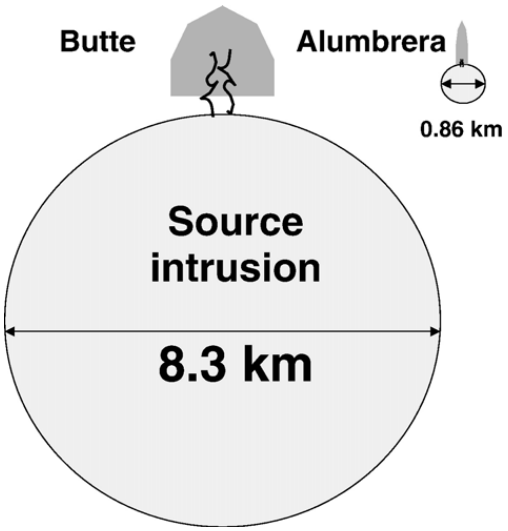

Fig. 7. Sizes of the zones of potassic alteration and the magma bodies required to supply the magmatic volatiles needed to produce it at Butte and Alumbrera. Large deposits require devolatalization of large magma bodies.

how the ratio of Na^+ to K^+ depends on temperature when the fluid is buffered by Na- and K-feldspars. Assuming the concentration of Na^+ does not change, his Fig. 4 suggests the equilibrium concentration at 500 and 600 °C will be about 60% and 70% of the total concentration at 800 °C. One potassium complex is likely to dominate. Geochemical calculations at 590 °C show that ~80% of the potassium is in the KCl complex (Reed, p.c., 2007). Thus the most appropriate value of f is 0.3. If there were three potassium species of roughly equal concentration f would be 0.1, but this is not the case.

We assume that the aqueous potassium complexes diffuse through pore waters with the harmonic mean of all the diffusivities of the solution species likely to be present at 400 °C as calculated from the Stokes–Einstein (Cussler, 1997) relation by Geiger et al. (2002). We have increased Geiger et al's diffusivity by a factor of 2.34 to account for the difference between the temperature they consider (400 °C) and the 600 °C we consider. Thus we take $D=1.19$ m^2/yr.

We have assumed a base value of connected porosity $\phi=0.005$. Studies relating to the long term storage of radioactive waste have provided a number of recent measurements. By impregnating samples in situ Schild et al. (2001) found the connected porosity of the Grimsel granodiorite in the Central Swiss Alps, before stress release produced additional micro-cracks, was between 0.4 and 0.5%. The connected porosity after stress release was 2 to 2.5 times greater. By compressing rock samples from the Illinois UPH3 drill hole to greater than in-situ effective stress Morrow and Lockner (1997) placed an upper bound on connected porosity of ~0.4% for this granite. Nelson and Rachiele (1982) analyzed 21 intact core samples and determined that the interconnected matrix porosity of the Stripa quartz monzonite in Sweden was 0.46%. Helium porosimitry on 6 samples yielded an interconnected porosity of 0.3%. Sardina et al. (2006) investigated the effect of deformation on connected porosity in the Kivetty granodiorite in Finland, showing that natural deformation increased the connected porosity from ~0.16% to 1.14%. Thermal stresses (the differential thermal expansion or contraction of mineral grains) are thought to produce the general (background or unsheared) matrix porosity (Geraud, 1994). Since the intrusive rocks that host porphyry deposits are heated by the fluids that produce the potassium silicate alteration, they are thermally stressed. They must also have been deformed to some degree by the intense hydrofracturing that accompanied the potassium silicate alteration. Thus a porosity of ≥0.5% can be expected. However, it is possible that at temperatures of >600 °C the porosity in the zones around grains will be annealed to some degree. Thus we consider a range of effective porosity of 0.1 to 1%, while adopting an expected value of 0.5%. Porosity changes during alteration were minimal for the acid halos modeled by Geiger et al. (2002) and should be even less for the potassium silicate alteration.

We assign the value of pore tortuosity/constriction using an empirical relationship that Geiger et al. (2002) determined from data compiled by Ohlsson and Neretnieks (1995): $\tau = \frac{D}{D_E} = \frac{0.68}{\phi^{0.72}}$. As noted above, our τ takes into account both the tortuosity of the diffusion pathways and constrictions in them. It converts connected porosity into effective diffusional porosity. Effective diffusional porosity is that porosity which, when multiplied by D, gives the diffusional flux of chemical species through the rock matrix.

Geiger et al.'s relationship gives $\tau=7$, 11, 19, 30, and 100 for $\phi=4$, 2, 1, 0.5, and 0.1%. It appears to work quite well, not only on the data compiled by Ohlsson and Neretnieks (1995), but also in other data sets. For example Cathles and Apps (1975) used $\tau=5$ to successfully model the development of copper-free halos on rock fragments with 4% porosity in Bingham porphyry copper waste dumps. Centimeter leach rims develop on these fragments in a few decades at ~40 °C. Norton and Knapp (1977) ran diffusion experiments on rock wafers and determined that τ for Butte quartz monzonite samples with a total (including unconnected) porosity of 6.35 and 1% were 10 and 42 respectively. If based on the unconnected porosity alone, these tortuosity predictions would be reduced. For $\phi=0.5\%$, the most likely value at Butte, $\tau=30$, and we adopt this as our base case value. If $\phi=0.1\%$ or 1%, τ would be 100 or 19.

From core measurements we have made, the vein density at Butte varies from 10 veins per meter of core up to more than 60 veins/m. On average the number of veins per meter is ~22 and this average changes very little over a radial distance of ~1500 m. Based on this fracture frequency, the vein half spacing S would range from 0.008 to 0.05 with a mean of 0.023 m.

The complex cross-cutting nature of porphyry veining indicates that not all the veins are open at the same time. This is taken into account with the factor f_{active} in Eq. (14a,b). If one third of the veins in the host today were active at any one time, $f_{active}=0.33$. If 10% of the veins were active at any one time $f_{active}=0.1$.

The parameters not discussed, such as the abundance of original hornblend, or the radius of pervasive alteration are observational parameters that can be evaluated by the reader from the discussion already given. The impact of changing any parameter relative to the base case (bold numbers in Table 1) can be evaluated by

inspection of Eq. (14b). For example, if 10% of the veins were active at any one time rather than the 30% we assume in our base calculation, f_{active} would be decreased by a 3rd and $t_{venting}$ increased by a factor of 3. If the vein S spacing were 5 cm rather than 2.3, the duration of venting would be increased by a factor of 5/2.3=2.2. Note that the vein spacing is related to the fraction of veins that are active at any one time, and therefore these parameters should not be varied simultaneously.

Considering the range in f_{active} and ϕ/τ, the range in venting times for Butte is $281 < t_{venting} < 44{,}200$ yr with a most likely value of 888 yr. The time required to produce the potassium silicate alteration could be increased by a factor of 3 if 10% rather than 30% of the veins were actively flowing at any one time (e.g., $f_{active}=0.1$ rather than 0.3), and increased by a factor of 16.6 if the connected porosity of the matrix were 0.1 rather than 0.5% because ϕ/τ would be increased by a factor of 5 for porosity and 3.33 for tortuosity. On the other hand, if the effective porosity were increased by the thermal and shear stresses to 1%, ϕ/τ would be decreased by a factor of 0.32. The overlapping of veins suggests less than 30% were active at one time, and we therefore do not increase f_{active} above the base value. As show in Table 2 the corresponding range for Alumbrera is $6.3 < t_{venting} < 996$ yr with a most likely value of 20 yr.

6. Relationship between potassium silicate alteration and mineralization

Potassium silicate alteration is the most extensive alteration observed in porphyry systems (Titley, 1982). At Butte, as elsewhere, it extends well beyond the limits of the other alteration styles (Fig. 5). This, and the fact that it is the hottest alteration, suggests the early venting was the most rapid and that the system cooled as the venting subsequently waned. Also the host environment was clearly initially less permeable than was required for the release of the magmatic volatiles, and the lithostatically-pressured volatiles created permeability by hydrofracturing the host. The veinlets that ultimately were so numerous as to have a separation of only ~5 cm (=2S) were produced by hydrofracturing.

A number of workers have argues that the stages of alteration in porphyry copper systems are related to changes in temperature. The early potassium silicate alteration at Butte and other porphyry systems such as El Slavador is associated with irregular, discontinuous, and deformed (non-planar) veinlets that contain biotite, quartz, and K-feldspar. This alteration represents the addition of potassium to the rock when the rock was very hot and still plastic (>600 °C). It is followed by veins that contain ore minerals and within which potassium minerals were neither destroyed nor precipitated, and then by veins (illustrated in Fig. 1) that show feldspar dissolution and have gray sericite or sericite–chlorite halos produced by acid attack which formed at temperatures of 400 to 450 °C (Rusk et al., 2004). The early potassium silicate veins can be seen to connect to aplite veinlets, e.g., directly to magma. (Gustafson and Hunt, 1975; Rusk et al., 2004; Seedorff et al., 2005; Brimhall, 1973; Rusk and Reed, 2004; Reed, pc, 2004). Reed et al. (2002; see also Dilles et al., 2004) and Rusk et al. (2004) have argued that all these veins were produced by the same magmatic fluid. Aplite veinlets lost water and became the conduits for aqueous volatiles. As the magmatic fluid cooled, HCl dissociated and SO_2 disproportionated into H_2SO_4 and H_2S (Seedorff et al., 2005). The fluid became acidic, and acid (sericitic) alteration was superimposed on the earlier potassium silicate alteration. The increased H_2S concentration raised the concentration of HS^- which caused the precipitation of sulfides, and ore minerals such as chalcopyrite became important vein minerals. In this view the potassium silicate alteration is just an early aspect of an evolving fluid expulsion event.

The volume of magmatic fluid required to produce the potassium silicate alteration at Butte is much more than sufficient to heat this same volume of host to >600 °C. The heat capacity per unit volume of magmatic fluid with density 400 kg/m^2 is about the same as water-saturated host. Thus, roughly one volume of magmatic volatiles equal to the volume of potassically altered rock would be needed to raise its temperature from ambient to that of the source volatiles. The volume needed to potassically alter the host is 22 times bigger than this ($\bar{G}$ in Table 1). If the initial venting was rapid, the thermal front would move out from the vent at a much faster rate (22 times faster) and much further ($\sqrt{22}\approx 4.7$ times further for cylindrical venting) than the potassium silicate alteration front. The potassium silicate alteration front that we have been discussing would thus move isothermally through host rock that had been heated to >600 °C.

Once the venting waned sufficiently, the heated volume of rock would begin to cool. How rapidly it could cool depends on several factors, the most important of which are probably the permeability of the distal host and the degree to which the rate of venting waned. If the host rock in the more distant parts of the heated zone is permeable, the cooling could be assisted by pore water convection and therefore could be more rapid. If the distal host was impermeable, the cooling would need to be by conduction only. If the venting rate

had slowed to the point it was not effective in keeping the system warm, we can estimate now long this kind of cooling would take. Butte is thought to have formed 4 to 9 km below the surface (Rusk et al., 2004). The time to cool to this depth is about $d^2/4\kappa$, where d is the depth and κ is thermal diffusivity. Taking $d=4$ to 9 km and $\kappa=10^{-6}$ m^2/s given $t=127{,}000$ to 642,000 yr.

It is important to appreciate that the center of the Butte system must have been at ~600 °C for the entire period over which magmatic volatiles were venting. It could never have cooled. The central areas of Butte show no minealization or acid alteration, a point we initially missed until it was re-emphasized to us by Mark Reed (p.c., 2007). Sulfide deposition and acid alteration will be produced if flowing magmatic volatiles are cooled to ~550 to 400 °C. If this had occurred in the core of the Butte pre-main stage system at least some veins there would contain metal sulfides and have acid alteration halos. The lack of mineralization and lower-temperature alteration in the core of the Butte system thus means that it cooled after the release of magmatic volatiles had ceased. This supports the notion that a single stage of volatile release was responsible for the pre-main stage Butte mineralization, and shows how estimates on the time required to cool the core of the system gives some measure of the duration of the entire mineralizing event. If distal pore water convection did not accelerate the cooling process and continued venting did not significantly retard the conductive cooling, mineralization at Butte could have occurred over a period of 100 to 500 thousand years.

The rate of volatile venting undoubtedly varied over the pre-main mineralization stage of volatile release. How much could it have varied? The regularity of alteration and mineralization zoning is one of the most remarkable characteristics of porphyry mineralization (Fig. 5), and this regularity suggests the variations could not have been too extreme. If, following the major volatile release that produced the potassium silicate alteration, there were episodes of volatile release widely separated in time and of strongly disparate intensity, it is hard to see how the geometry of the alteration could be so regular, and hard to see how the general thermal progression of the alteration could be as regular as observed. Higher and lower temperature alteration and veining should be mixed irregularly in a single vein, for example. The simplest inference is that the episodes (modulations) of volatile release were frequent and regular and died out in a fairly smooth fashion.

At Butte there were probably two main volatile release events: The first, which we analyze in this paper, occurred between 66.4 and 64.8 Ma and is associated with the pre-main stage of mineralization. The second produced the meter wide ore veins of the main stage mineralization, which, according to radiometric dating, occurred between 65 and 62.5 Ma (Dilles et al., 2003). Separate intrusion events are a logical way to produce these two volatile release events and their associated mineralization (Seedorff et al., 1975). The pre-main stage release was effectively contained, and a very regular alteration and mineralization pattern was produced. Broad venting along a 7 km axis produced the potassium silicate alteration. Centers of porphyry mineralization developed at the Pittsmont and Anaconda Domes as the venting waned (Fig. 5). The second, main stage, volatile release event was less well contained, and the system ruptured along major faults. Volatile expulsion through these faults produced the spectacularly-wide main stage veins.

For smaller, shallower porphyry systems with more saline magmatic fluids like Alumbrera, the duration of early venting is much shorter (~20 yr), the volume of rock heated to the temperature of the magmatic volatiles potentially only about as big as that potassically altered host ($\sim\bar{G}=1.35$), and the time to cool much shorter $t\approx d^2/4\kappa=150^2/4\times10^{-6}\times3.15\text{E}7=180$ yr, where 3.15E7 is the number of seconds in a year). Potassium silicate alteration in such porphyries could be more mixed with the other kinds of alteration, and comparison between the potassium silicate alteration in low and high salinity magmatic systems could be an interesting research avenue to pursue.

7. Discussion

The time that we calculate was required to accomplish the early potassium silicate alteration at Butte and Alumbrera is remarkably short. For the minimum duration of ~300 yr in a very large system like Butte (6 yr at Alumbrera) the rate at which the magmatic volatiles were expelled is so fast that the process can perhaps be best described as a contained explosion. Is it plausible that the rate of volatile release could be this fast? We believe it is. Porphyry copper deposits that form over shallow magma chambers commonly blow up. Porphyries were destroyed in the recent Mt Pinatubo volcanic eruption (Hattori, 1996), for example. Sillitoe (1994) has emphasized that eruptions caused by sector failure are one of the risks to the formation of porphyry-type ore deposits (see also review by Richards, 2003). Mineralization during the Butte main stage produced ~3 m wide veins (and as wide as 10 m, and even 15 to 20 m where the veins were multiply opened) filled with ore. The width of these veins suggests they were very

permeable and flow through them rapid. Pebble dikes require volatile flow rates sufficient to tumble and round rock fragments. They are common in and near porphyry deposits (c.f., Gustafson and Hunt, 1975; Perello et al., 2003). Breccia pipes are also common. These can form by collapse of fluid-filled cavities (Norton and Cathles, 1973) or by explosive expulsion of volatiles. Eruptions can occur in a few days, so it is not unreasonable that controlled volatile venting might occur over a few years or centuries.

The venting duration we derive from the potassium silicate alteration pattern has a certain necessity to it. There must be a transition from fully altered to fresh host. The volume of altered host certainly measures the volume of reactive fluid expelled. The width of the transition from fresh to altered host must depend on (and measure) the rate of volatile expulsion. Our estimate of the duration of venting does, however, rest on three critical assumptions: that the rate of alteration is controlled by diffusion across the vein halos (gives us time control), that the flow of the magmatic volatiles is approximately perpendicular to the boundaries of the alteration (so the transition is a reaction front), and that the alteration occurred broadly as the result of a single volatile release (i.e., not as the result of a complicated and highly episodic set of separate fluid squirts).

The assumption of diffusion control of the potassium silicate alteration is confirmed by the observations that the reaction zone separating the halo from fresh rock is only 2 to 4 mm and is characterized by biotite rimming hornblende (Dilles, pc., 2007; see also Seedorff et al., 2005), exactly as expected (Cathles and Apps, 1975). Flow was almost certainly roughly perpendicular to the alteration boundaries. The zoning of mineralization and alteration in porphyry systems suggests this, and outward radial flow from the axis where lithostatically-pressured magmatic volatiles are introduced is physically expected. The last criterion (a single major stage of volatile release) is required by the regularities of heating and alteration as discussed above.

An initially rapid, almost explosive, expulsion of volatiles is compelling because it offers an explanation for the observation that potassium silicate alteration is more extensive than mineralization and acid alteration. It logically connects the disseminated, well zoned, and geometrically regular alteration that is so characteristic of many porphyry deposits and the wide veins that develop in some. It emphasizes further the vulnerability of porphyry deposits to explosive destruction. And it is interesting because it suggests that there could be minor chemical signatures that extend well beyond the outer limits of potassium silicate alteration, and that the far-field permeability may control important aspects of the mineralization process. A permeable host might allow the accumulation of more metal because less of the metal-rich volatiles would escape the system without cooling sufficiently to precipitate their metal content, for example.

How could a body of magma release its volatiles in a period as short as 300 (or 6) years? The temperature at which a "wet" magma (i.e., a magma that contains dissolved water) begins to crystallize is greater than the temperature at which a dry (water free) magma is entirely crystallized. Thus, if pressure is reduced so that water is released from a water-rich magma, the magma can freeze and expel its volatiles very rapidly in a process called second boiling. For large bodies, rapid quenching could be inhibited by the ~2721 kJ/kg heat released by the crystallization process (Norton and Cathles, 1979). Crystallization might then proceed only at the rate at which heat could be removed from the system. This did not restrain the rapid eruption of the 800 km^3 Bishop Tuff , but it could modulate the release of volatiles from magma bodies that are not physically excavated by eruption. On the other hand, volatiles may accumulate slowly at the top of a magma body, and then vent rapidly. But if this is so, it is surprising that such a large fraction of the volatiles from so large a body of magma would collect and release all at one time. One would expect a more frequent and more spatially complex (e.g., a series of breccia pipes) release of ponded volatiles.

Our estimates of the rapidity of the initial release of magmatic volatiles could be tightened or supported in a number of ways. The duration of venting could be tightened if, from cross-cutting relations, it was possible to determine the fraction of veins that were active at any one time. Confidence in our interpretation of the width of the transition from fully potassium silicate altered to fresh host would be increased if the veins spacing were wider where the transition width is wider. For example, for a constant $t_{venting}$, Eq. (14a,b) suggests that Δr will be larger where S^2 is larger in a compensating fashion. It would be very nice to have a better handle on ϕ/τ during the mineralizing event. For this, the effects of thermal and minor mechanical stress need to be better understood. If we knew the kinetics of potassium silicate alteration, the observed widths of the reaction zone at the edge of the potassium silicate alteration halos could be used to constrain ϕ/τ during alteration following the methods in Cathles and Apps (1975). Thermal modeling could provide an indication of how rapid the initial venting would have to have been to fully heat the potassium silicate alteration zone, and how much the rate

of venting would need to diminish for the system to cool sufficiently to allow base metal deposition and acid alteration.

8. Conclusions

This paper defines and applies relationships that must exist in a diffusion-controlled vein–halo–style alteration of a uniformly fractured host between the radius of pervasive alteration, the width of transition from fully altered to fresh host, and the total volume and rate of expulsion of the altering fluids. The volume of alteration measures the total volume of reactive fluid expelled through the host, and the width of the transition from pervasive to no alteration measures the rate of fluid expulsion. Division of the two gives the duration of the fluid expulsion. These systematics are captured by mathematical equations which can be very easily applied to diverse geological situations. Application to the early potassium silicate alteration that occurred in two porphyry systems of quite different size suggests that this alteration occurred when 0.01 (Alumbrera) to 100 (Butte) km^3 of magmatic volatiles vented in ~20 and ~900 yr, respectively. Parameter uncertainties allow these estimates to be increased by at least a factor of ~50 or decreased by at least a factor of ~3. We argue that the other kinds of alteration and mineralization that are associated with the potassium silicate alteration occurred as the venting waned and the system thermally collapsed. During the collapse, pulses of fluid expulsion declined in intensity in fairly smooth fashion over a period that, for pre-main stage Butte, might have been ~100,000 to 500,000 yr.

Porphyry copper systems such as Butte and Alumbrera seem to begin with the venting of large volumes of volatiles in a very short interval of time in a process that can, at its extreme, be described as a barely-controlled devolatilization explosion. This expulsion intensely fractures the surrounding host, produces extensive potassium silicate alteration, and heats an even larger host volume to ~600 °C. As the venting wanes and thermally collapses, metals are deposited and smaller, but still geometrically very regular, ore shells are formed (e.g., the Pittsmont and Anaconda Domes at Butte). The style of mineralization depends on the stress field, perhaps especially at the time of the initial, explosive volatile release. A second major episode of volatile venting at Butte opened a few major structures rather than many hydrofractures. The spectacularly-wide main stage veins at Butte were the result. The extensive potassium silicate alteration, the smaller domal porphyry mineralization with their regular alteration pattern, and the occasional formation of spectacularly wide veins are easier to understand if viewed in the context of an initial, voluminous, and almost explosive volatile release after which the venting rate strongly diminishes. A rapid initial release raises many interesting questions regarding how magmas devolatilize and how the process can be controlled so that an ore deposit can be produced, suggests the exploration target for large porphyry deposits may be much bigger than the area of potassium silicate alteration, and suggests that far field permeability may be important. The analysis illustrates the power and stimulating nature of very simple semi-analytic mathematical models that capture mass balance relations on both the local and system scale.

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