Deep Fluid Circulation and Isotopic Alteration of The Geysers Geothermal System: Profile Models

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Abstract

Unusual rock alteration patterns related to felsic intrusives (felsite) at The Geysers are important indicators of the origins of the modern geothermal system. The Geysers show widespread moderate oxygen isotope alteration in the permeable steam reservoir above the felsite, with maximum alteration low on the flanks of the felsite. Numerical models of fluid, heat and oxygen isotope transport in the pre-development (natural state) Geysers system demonstrate that an unbroken caprock is required throughout the liquid-dominated lifetime of the system to produce this pattern. In addition, moderate depletion of whole rock $\delta^{18}O$ values throughout the greywacke steam reservoir suggest a long-lived liquid system. The distribution of these moderate values is most consistent with rapid cessation of fluid circulation soon after maximum temperatures were reached in the upper reservoir. The models indicate the maximum hydrothermal lifetime for the system is 0.5 million years (Ma), while the youngest dated intrusive is around 1 Ma. Combined, these factors indicate repeated igneous intrusions at The Geysers, up to at least 0.5-0.6 Ma ago, development of a stable liquid-dominated system after that, the evolution of which was truncated by a relatively recent transition to vapor-dominated conditions. Observed chemical compartmentalization of fluids in The Geysers steam reservoir is inconsistent with the lateral extensiveness of alteration at depth, since the latter requires good horizontal connectivity of deep permeable zones to allow penetration of ^{18}O-depleted fluids. This compartmentalization is probably recent, developing as a consequence of vapor-dominated conditions introducing relative permeability effects. Petrologic evidence for high paleo-fluid temperatures (300 °C) within 1 km of the surface is difficult to reconcile with subdued ^{18}O alteration at depth beneath those locations. These high-temperature veins are likely to indicate small, short-lived penetrations of the caprock. Natural-state models allow the combined influence of these factors on the evolution of The Geysers to be analyzed quantitatively. The significant results are most clear in graphical animations, Internet-accessible examples are available at http://www.utdallas.edu/~brikowi/Publications/Geysers.

Key words: geothermal, The Geysers, hydrothermal, model, O-18 alteration,

1 Introduction

The Geysers offer a unique opportunity in the U.S. to study an active hydrothermal system where the plutonic heat source is accessible. Natural state modeling of this system uses system-wide fluid mass and heat balances in space and time to derive a general view of system characteristics, evolution and lifetime. The benefits of such an approach at The Geysers are synthesis and advancement of our understanding of the nature and development of this important geothermal resource based on fundamental physical principles. This paper describes results of fluid and heat flow models for the pre-boiling state of The Geysers, including quantitative constraints on the hydrothermal system derived from vein-mineral geothermometry and observations of rock isotopic alteration. The analysis begins from a geologically known condition, the initial appearance of the heat source (magma intrusion). From this starting condition, the models can calculate the dissipation of the original thermal and chemical energy of the intrusion into its host rocks. The models compute the temperature, pressure, fluid flow and chemical ($\delta^{18}O$) composition field for The Geysers geothermal/hydrothermal system from the time of its inception (magma intrusion) to a time immediately prior to boiling. These models are also constrained (calibrated) using the current state of the system, including the temperature and pressure fields, distribution of chemical and isotopic alteration, and distribution of fractures and permeability. Since the liquid phase is most efficient at isotopic alteration, observed alteration provides strong constraints on the pre-boiling state of The Geysers, and little direct constraint on the post-boiling state.

The Geysers system may best be viewed as a plutonic hydrothermal system whose development has been profoundly impacted by shallow depth of intrusion and low permeability host rocks. The Geysers exhibit many of the features found in fossil plutonic hydrothermal systems, including development of a low-permeability caprock above a more permeable altered zone. Alteration in the underlying intrusive is concentrated at its margins. The distribution and nature of these features at The Geysers differs significantly from typical fossil examples (e.g. copper porphyry systems, Lowell and Guilbert, 1970; Gustafson and Hunt, 1975), giving important clues as to the nature and evolution of The Geysers hydrothermal/geothermal system. In particular, fossil hydrothermal settings typically exhibit the most intense alteration in an extensive vertical

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zone directly above the apex of the intrusive heat source. Paragenetic relationships suggest breaching of the caprock typically occurs late in the history of these systems. The Geysers show the greatest alteration low on the flanks of the intrusive heat source (felsite), and only minor penetration of the caprock. The models described below demonstrate that these features require reduced fluid circulation above the apex of the felsite throughout the liquid-dominated history of the system. This is most readily achieved by preserving the integrity of the caprock. In the case of The Geysers, low fluid recharge rates and shallow depths presumably led to widespread boiling (and cessation of significant rock alteration) before the caprock was disrupted as in more typical systems.

1.1 Geologic Setting

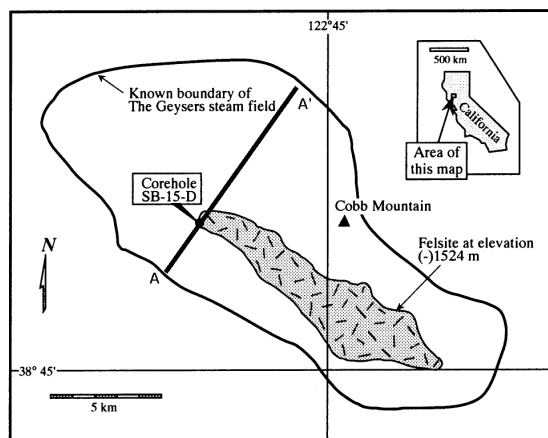The Geysers (Fig. 1) is one of a few productive vapor-dominated systems in

Fig. 1. Location of Geysers steamfield, felsite and model cross-section (after Hulen and Moore, 1996). Coring project well SB-15d and location of model cross-section (A-A') shown near center of steam field

the world, and currently produces approximately 840 MWe from a 150 km^2 area. The system has been extensively explored and developed, with data available from some 780 deep wells, many penetrating the underlying plutonic heat source. The Geysers system is developed in a structurally complex collection of Jurassic to Cretaceous metamorphic rocks, primarily metagreywacke, forming the Franciscan Complex (Fig. 2). Pleistocene intrusion of felsic rocks, collectively termed "felsite" (Schriener and Suemnicht, 1980; Thompson, 1992), provided the heat and reservoir permeability for the system. The felsite intrusive is found as shallow as 0.7 km depth in the southeastern Geysers, with minimum radiometric ages of around 1.2 Ma (Dalrymple *et al.*, 1999; Hulen *et al.*, 1997). The geometry of the felsite top is relatively well characterized, and has been described in a variety of publications (Hulen *et al.*, 1994; Hulen and Nielson, 1996). Permeability was generated in the roof rocks of the intru-

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sive by hydrothermal dissolution of earlier metamorphic vein carbonate, and thermal fracturing in the upper felsite (Hulen and Nielson, 1995). A caprock is present, distinguished by undissolved metamorphic calcite and younger vein-filling calcite apparently related to the modern hydrothermal system. This system has left a strong alteration and metasomatic signature, forming a distinctive tourmaline-bearing hornfels along the contact of the felsite, and marked depletion of whole rock $\delta^{18}O$ along the lower flanks of the felsite (Fig. 2, lower portion).
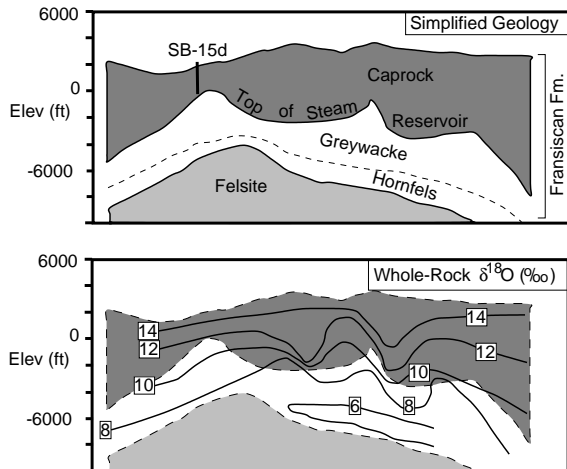

Fig. 2. SW-NE cross-section of The Geysers, passing through well SB-15d, showing simplified geology and whole-rock $\delta^{18}O$ alteration (after Hulen *et al.*, 1994). Location of SB-15d and cross-section line shown in (Fig. 1).

1.2   Model Scenario

In order to study general aspects of the development of this complex, active, and incompletely characterized system, a number of simplifying assumptions will be adopted. System permeability will be assumed to be purely a function of lithology, and invariant with time. The present-day distribution of the steam reservoir (i.e. zone of borehole steam entries) is used as an initial estimate of the distribution of caprock and permeable zones above the felsite. Modern fluid isotopic and non-condensable gas compositions have been cited as evidence of compartmentalization (i.e. fault zones forming impermeable barriers) between the Northwestern and main Geysers steam reservoirs (Walters *et al.*, 1996; Truesdell *et al.*, 1995). The area chosen for modeling is well south of these proposed barriers. The felsite will be treated as a single, instantaneous intrusion, with no additional heat input into the system.

The models will aim to match observed alteration and paleotemperature indicators. Petrologic constraints on paleotemperatures are available from drilled core and cuttings (Hulen and Nielson, 1995; Moore *et al.*, Oct. 1989). Moore

and Gunderson (1995) have outlined the distribution of $\delta^{18}O$ alteration at The Geysers, finding an 8‰ decrease in rock $\delta^{18}O$ along the felsite-greywacke contact (Fig. 1). Similar observations have been made for the Northwest Geysers (Walters *et al.*, 1996). Isotopic exchange rates will be assumed to be functions of temperature and initial lithology, the effects of mineral dissolution/deposition and transient surface area changes will be neglected.

1.3 Model Geometry

In order to investigate the basic time and length scales for hydrothermal circulation at The Geysers using system-wide mass and heat balances, preliminary finite difference models of heat and fluid flow were made (Brikowski and Norton, 1999; Hulen and Norton, 2000, this volume). Modeling was carried out over a two-dimensional cross-sectional grid oriented SW-NE passing through Geysers Coring Project well SB-15d, and extending 10.8 km horizontally and 5.4 km vertically (see line, Fig. 1). Permeability zones were based on current distributions of steam reservoir and felsite (Fig. 2); a single instantaneous intrusion of granodiorite was assumed for the heat source. Caprock thickness was increased 20% over present values to account for erosion. Consequently, boiling conditions were not present in the reservoir and felsite in this model. Based on the finite difference analysis, solutions of heat, fluid and isotope transport were obtained using a finite element discretization (Fig. 3) of the same section (Fig. 2). The section is assumed to have insulating, impermeable sides everywhere but the top. The finite element results are described in detail below.

2   Governing Equations

The governing relationships for heat and fluid transport are well established, and will not be developed here (see Norton, 1984; Pruess, 1991). Isotope transport can be modeled using the standard advection-dispersion equation, with minor variations in choice of variable and treatment of chemical reaction. Analytic solutions to the simplified chemical transport equation expressed in terms of rock isotopic ratio R have been utilized to constrain ratios of transport parameters (Cook and Bowman, 1994). The models described below were developed in terms of $\delta^{18}O$, the isotope ratio normalized to a standard, in order to simplify comparison to observations reported as $\delta^{18}O$. A similar development is detailed by (Norton and Taylor, 1979). For simplicity rock reaction is treated as exchange with the fluid by a single solid phase. The advection-dispersion equation (i.e. mass balance for ^{18}O) for such system can
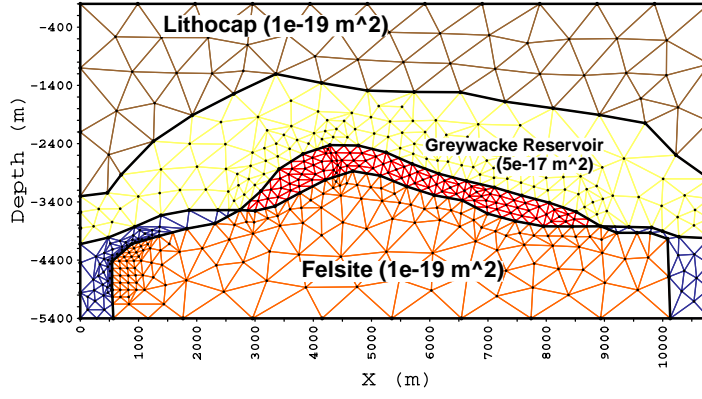
Fig. 3. Finite element model grid, showing lithologic zones and modeled intrinsic permeability. Bottom of well SB-15d is located approximately at the highest point of the steam reservoir-lithocap contact. The model contains 1071 quadratic triangular elements and 2188 nodes.

be written as (Bear, 1979, eqn. 7-42)

$$\underbrace{\frac{\partial(\phi\rho C)_f}{\partial t}}_{\text{Liquid Composition}} = \underbrace{-\nabla\cdot[\phi_f\mathbf{D}\nabla(\rho C)_f]}_{\text{Dispersion/Diffusion}} - \underbrace{\nabla[\vec{q}(\rho C)_f]}_{\text{Advection}} - \underbrace{\frac{\partial(\phi\rho C)_r}{\partial t}}_{\text{Rock Composition}} + \quad (1)$$

The concentration variable C_i (mass of ^{18}O in phase i per unit volume of rock) can be expressed in detail using the definition of δ^{18}O:

$$C_i = \nu_i\left(\frac{\delta^{18}O_i}{10^3} + 1\right)\cdot R_{standard} \qquad (2)$$

where ν_i is the mass of exchangeable oxygen in phase i. Then (1) can be rewritten as

$$\frac{\partial(\phi\rho\nu\delta^{18}O)_f}{\partial t} = \nabla\cdot[\mathbf{D}\nabla(\phi\rho\nu\delta^{18}O)_f] - \nabla[\vec{q}(\rho\nu\delta^{18}O)_f] - \frac{\partial(\phi\rho\nu\delta^{18}O)_r}{\partial t}(3)$$

The equation describing water-rock exchange of ^{18}O in a system is assumed to follow a first-order rate law (Gregory *et al.*, 1989, eqns. 9-10)

$$\frac{\partial R_i}{\partial t} = k_{if}(\underbrace{\alpha_{if}R_f}_{\text{equilibrium }R_i} - \underbrace{R_i}_{\text{actual }R_i}) \qquad (4)$$

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where R_i is the ^{18}O/^{16}O ratio for the ith phase. This can be converted to δ notation by observing that

$$\delta_i^{18(eq)} = \delta^{18}O_f \ + \ \Delta_{if}$$
$$\Delta_{if} \equiv \frac{A}{T^2} + B$$

Then (4) becomes

$$\frac{\partial \delta^{18}O_r}{\partial t} = k_{rf}(\delta^{18}O_f \ + \ \frac{A}{T^2} \ + \ B \ - \ \delta^{18}O_r) \tag{5}$$

where the term on the left is the change in δ^{18}O with time in the ith reacting mineral in the volume of interest, k_{if} is the kinetic exchange coefficient between that mineral and the fluid (units $\frac{1}{\sec}$) modeled using an Arrhenius relationship (i.e. thermally activated, Cole and Ohmoto, 1986). Δ_{if} is the equilibrium δ^{18}O difference between mineral i and fluid at current temperature and pressure. Then exchange between minerals and fluid is proportional to the reaction rate (which is strongly proportional to temperature) and the compositional difference between the current assemblage and a hypothetical one at equilibrium. Equation (5) describes the source/sink term in the standard advection-dispersion equation for transport of ^{18}O. Substituting this expression for the right hand term of (3) obtains the final form for the ^{18}O mass conservation equation used in this study:

$$(\nu\phi)_f \frac{\partial(\rho\delta^{18}O)_f}{\partial t} = \ \nabla \cdot \mathbf{D}\nabla(\nu\phi\rho\delta^{18}O)_f \ - \ \vec{v} \cdot \nabla(\nu\rho\delta^{18}O)_f$$
$$- \ (\nu\phi\rho)_r \ k_{rf}(\delta^{18}O_f + \frac{A_r}{T^2} + B_r - \delta^{18}O_r) \tag{6}$$

This equation can be solved using finite difference or element methods. A much-modified version of the finite-element program Mariah (Brikowski and Norton, 1989; Brikowski, 1995) was used to model the system governed by this and the heat and fluid flow equations.

3 Model Results

Two-dimensional models of heat and fluid flow and ^{18}O transport were made using a finite element model over the cross-section depicted in Figure 2. To allow for maximum solution stability, grid density was concentrated where high

advection and reaction rates were anticipated (Fig. 3). The top boundary of the model was held at constant temperature and pressure, model sides and base were treated as impermeable and insulating. Owing to the dominant effect of the impermeable lithocap, permeable or impermeable side conditions had little effect on the solution. Repeated model runs were made, adjusting parameters (calibrating) until an adequate fit was achieved to observed $\delta^{18}O$ alteration, geothermometers, and general constraints on surficial heat flow in the system. Details of the transfer function for isotopic exchange between fluid and mineral are poorly constrained (e.g. mineral reactive surface area), and therefore the results should be viewed in terms of average transfer rate. In fact this approach to model calibration leads to good constraints on time-integrated ratios of reaction to advection (Damkohler number) and diffusion to advection (Peclet number) rather than the values of the individual parameters making up those ratios.

3.1   Heat Transport and Fluid Convection

Model results demonstrate a number of fundamental features of The Geysers hydrothermal system. Perhaps of greatest significance are constraints on system lifetime. Purely conductive models of the geometry shown in Figure 3 indicate a maximum lifetime of 0.5 Ma, convective models using the indicated permeabilities reduce this lifetime to 0.35-0.5 Ma (Fig. 4a). The youngest dates available for the felsite are 1.2 Ma (Dalrymple *et al.*, 1999; Hulen *et al.*, 1997). This discrepancy indicates that The Geysers natural state system has had a considerably more complicated intrusive and hydrothermal history than is generally assumed. Similar conclusions have been reached by other authors based on geophysical analysis (Stanley and Blakely, 1995) and crustal-scale conductive thermal models (Dalrymple *et al.*, 1999).

Convection in the system is tightly constrained along the upward-sloping flanks of the felsite (vectors, Fig. 4). The lower boundary of this flow zone is controlled by the permeability contrast between reservoir and "basement felsite" rocks. The upper margin of this zone is formed by localization of near-critical fluid properties. Recall that heat transport and fluid flow properties reach extrema near the fluid's critical point (374°C and 22 MPa for pure water). These properties are computed in the model using an accurate numerical equation of state (Johnson and Norton, 1991). Heat capacity reaches near infinite values at the critical point, and is a useful indicator of near-critical conditions. A mantle of near-critical conditions develops in the host rock in the vicinity of the 375°C temperature contour (Fig. 4b). This contour moves outward from the felsite until around 125 thousand years (Ka), at the peak of hydrothermal activity, and then slowly retreats downward. By 240Ka critical conditions are within the deep, low-permeability felsite, and effective hy-
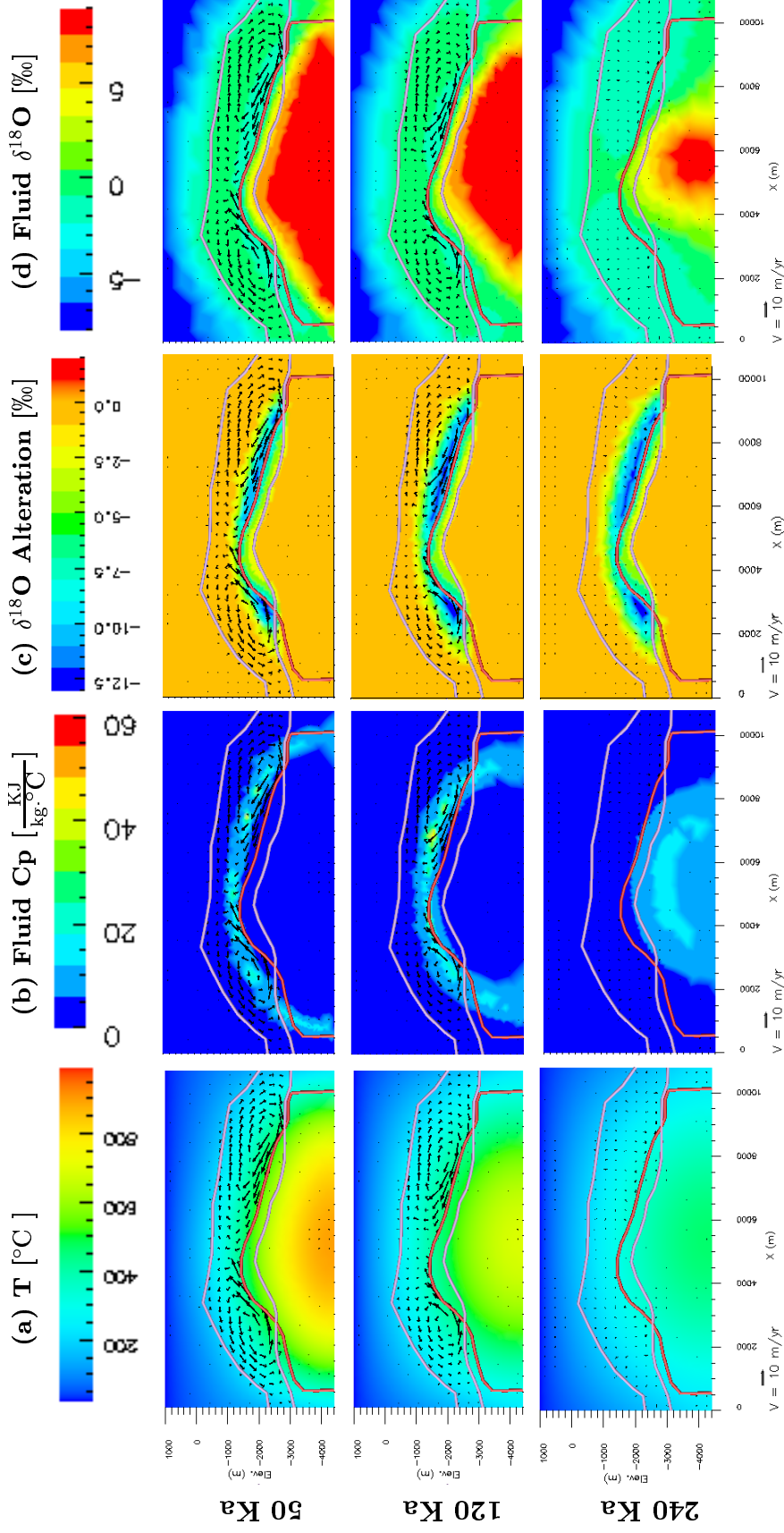
Fig. 4. Temperature (column a), fluid heat capacity(b), water and plagioclase $\delta^{18}O$(c & d) for 50Ka, 120Ka and 240Ka (rows). Shaded contour scales given at top of columns. Black vectors show flow direction, length proportional to velocity; see scale arrow at base of columns. Distance scale given at base of columns, no vertical exaggeration, each panel is 5.4 km deep and 10.8 km wide. Felsite boundary shown by red line, steam reservoir boundary by white lines. Whole rock equivalent alteration is 0.3-0.5 times the values in column (c).

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drothermal circulation ceases in the system. Hydrothermal circulation above the apex of the felsite is limited by the presence of the caprock, requiring divergent flow in that area, and by sub-critical fluid conditions within the greywacke reservoir there. Influx of meteoric water into the system is tightly channeled by these two phenomena, and is localized deep on the flanks of the intrusive. The net result of the permeability and fluid properties variations is to develop two circulation cells centered low on the flanks of the intrusive. Influx of fluid into these these cells is from the upper felsite reservoir. Models with permeable sides for the reservoir showed little difference, owing to the narrowing and deepening of the reservoir at the model boundaries, limiting horizontal fluid flow. The high variability of fluid Cp within the critical zone (Fig. 4b) reflects true chaotic behavior of critical T-P conditions in this regime (D. Norton, unpublished results).

3.2   Transport Model

To investigate the alteration impacts of this localized convection, the ^{18}O transport equation (6) was solved simultaneously with the heat and fluid transport equations. For simplicity, a single reactant mineral was assumed, effectively treating the system as two phases (liquid and solid) with only isotopic exchange and fluid advection allowed as chemical transfer mechanisms. In this way a bulk or equivalent transfer coefficient is obtained through model calibration, which reflects the combined influence of multiple exchanging minerals in the rock, of transient changes in mineralogy or reactive mineral surface area. The transfer direction and rate are treated as functions of temperature and phase compositions. Parameters for the rate law were derived from the following considerations. Average groundmass mineralogy of The Geysers host rock metagreywacke is approximately 40% quartz, 30% plagioclase (Moore and Gunderson, 1995). Lambert and Epstein (1992) note limited reaction of quartz grains in the greywacke, suggesting the primary reactant mineral is plagioclase. Volume fraction of plagioclase in rock was assumed to be 0.30, and volume fraction of mobile water in rock ϕ_f =1.0x10^{-3}. Isotopic parameters are the water-plagioclase isotope fractionation factor A = 2.61x10^6 and B = -3.7 (Javoy and Bottinga, 1973), unaltered rock $\delta^{18}O_r$ = 14‰ and maximum alteration $\delta^{18}O_r$ = 6‰ (Moore and Gunderson, 1995). Parameters for the Arrhenius formulation of the kinetic exchange coefficient were activation energy $\Delta E = 20000 \frac{cal}{mole}$, pre-exponential factor $A_o = 1.0$x10^{-6} $\frac{1}{sec}$. These values are consistent with averages summarized in Cole and Ohmoto (1986) and Lasaga (1981). The formulation gives an effective maximum transfer rate in the models of approximately 10^{-7} $\frac{moles\ O}{m^3\ sec}$, equivalent to 2.5–2.5x10^4 one cm^3 plagioclase crystals per m^3 rock at maximum reaction rates (Ω5.5x10^{-9}–5.5x10^{-9} $\frac{moles\ O}{m^2\ sec}$, Cole and Ohmoto, 1986).

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Alteration in the system begins quickly, with notable rock alteration visible by 20Ka. By 50Ka, depleted fluids have penetrated much of the way up the flanks of the felsite (top image, Fig. 4d). Because temperatures are high, rapid isotopic exchange is taking place, and the alteration progresses as a reaction front up the stream tube formed by the permeability contrast and critical-properties zone (Fig. 4c). As fluids approach the apex of the system, moving more sluggishly, they become enriched in $\delta^{18}O$ via exchange with the rock and no longer produce noticeable alteration. Had the caprock been permeable above the apex of the felsite, very strong convection would take place in that area, and a marked plume of ^{18}O–depleted fluids would alter the rocks in a vertical zone above the apex. The lack of such a pattern argues strongly for the presence of an unbroken caprock throughout the effective hydrothermal lifetime of The Geysers system. Although some vein material from well SB-15d support high fluid temperatures, this is not consistent with the lack of strong ^{18}O depletion in the shallow reservoir. Instead it seems that the SB-15d veins record small zones of penetration of the caprock that were geologically short-lived.

These alteration models, based as they are on a simplified view of The Geysers setting, do not completely match the observed moderate alteration throughout the reservoir (Hulen et $al.$, 1994; Moore and Gunderson, 1995). One possibility is to assume a larger kinetic factor k_{rf}, however doing so results in retrograde alteration (i.e. moderate re-enrichment of rock) by late-stage enriched fluids in the models. While retrograde mineralogic overprint is not uncommon in porphyry systems (e.g. the "phyllic overprint" of Gustafson and Hunt, 1975), petrologic evidence for this in The Geysers reservoir rocks is questionable. The Arrhenius parameters used in the models show here limit significant isotopic exchange to occur above 400°C . The upper portions of the reservoir reach a maximum of 300°C in a region where Hulen et $al.$ (1994) show whole rock depletion of 4-6 ‰. A possibility is that a larger kinetic factor is more appropriate, with the development of two-phase conditions (boiling) in the reservoir just after maximum temperatures were reached (and therefore maximum fluid energy for fracturing, Knapp and Knight, 1977), preventing retrograde alteration. A more probable alternative is that permeability differences let to higher fluid temperatures in the upper reservoir, allowing more complete isotopic exchange. Further modeling is underway to explore this alternative. In particular, constant permeability was assumed within the reservoir, in contrast to observations of decreasing porosity (and presumably permeability) with depth Gunderson (1990). Monotonically increasing permeability with distance from the felsite may provide a better match to observed alteration.

4 Conclusions

This initial analysis of the natural state of The Geysers, constrained in particular by observed $\delta^{18}O$ alteration reveals a number fundamental features of the system:

- low bulk permeabilities in the reservoir rock (0.05 md) are sufficient to allow the convective circulation of fluids required to produce observed alteration and vein mineralogies. These values are in general agreement with those determined in two-phase models of The Geysers steam reservoir (Pham and Menzies, 1993; Williamson, 1990)
- active hydrothermal circulation (given those permeabilities) persists for only 300 Ka after a single intrusion with the known geometry of the felsite
- enhanced heat and fluid transport related to critical fluid properties strongly focuses inflow and deep fluid convection into a "streamtube" along the felsite-greywacke contact
- isotopic rock alteration is strongly limited to the recharge zones of this streamtube, and becomes much weaker in the discharge zone of the streamtube near the apex of the felsite; hence maximum alteration is observed low on the flanks of the intrusive
- persistent integrity of the caprock is required to produce this pattern of alteration. Without the caprock, a vertical zone of strong alteration would be present above the apex of the felsite
- persistent horizontal hydraulic connectivity at depth is also required to preserve the streamtube effect along the low flanks of the felsite intrusive
- widely distributed moderate alteration within the reservoir supports one of several alternatives:
  - a long-lived liquid-dominated system, with boiling occurring soon after maximum temperatures are reached (about 100 Ka after felsite intrusion)
  - temperature-related deposition of minerals reduced permeability close to the felsite between 20-100Ka, allowing longer term alteration of the upper steam reservoir
  - isotopic alteration at The Geysers reflects the impacts of more than one intrusive and hydrothermal episode

The limited thermal lifetimes demonstrated here strongly indicate that the intrusive history of the felsite heat source at The Geysers is more complex than indicated by available age-dates. The rest of the features enumerated above are a consequence of this: factors limiting fluid circulation at The Geysers are responsible for the unusual thermal and alteration structure above the intrusive. Consideration of system-wide heat, fluid and ^{18}O mass balances at The Geysers allows a fundamental understanding of these features, and provides new insights regarding The Geysers as well as a firm basis for more focused reservoir engineering and production models.

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Table 1
List of Symbols

English Symbols	Meaning	Units
A, B	parameters in equilibrium constant formula	
C_i	chemical concentration (mass of ^{18}O in phase i	-
C_p	isobaric heat capacity	$\frac{\text{J}}{\text{kg}^\circ\text{C}}$
$\mathbf{D}$	dispersivity tensor	$\frac{\text{m}^2}{\text{sec}}$
k_{if}	kinetic exchange constant between phase i and fluid	$\frac{1}{\text{sec}}$
R	^{18}O/^{16}O ratio	-
T	temperature	$^\circ$C
$\vec{q}$	Darcy vector velocity	m/sec
t	time	sec

Greek Symbols		
α_{if}	isotopic fractionation factor between i and fluid	-
Δ_{if}	equilibrium isotopic fractionation between phases i and fluid	‰
δ^{18}O$_i$	normalized isotopic ratio in phase i	‰
ν	atomic mass fraction of oxygen	-
ϕ_i	volume fraction of i-th phase	-
ρ_i	density of i-th phase	$\frac{\text{kg}}{\text{m}^3}$

Subscripts	Meaning	
r	rock phase property	
f	fluid phase property	