Reactive flow of mixed CO₂–H₂O fluid and progress of calc-silicate reactions in contact metamorphic aureoles: insights from two-dimensional numerical modelling

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ABSTRACT

Previous models of hydrodynamics in contact metamorphic aureoles assumed flow of aqueous fluids, whereas CO₂ and other species are also common fluid components in contact metamorphic aureoles. We investigated flow of mixed CO₂–H₂O fluid and kinetically controlled progress of calc-silicate reactions using a two-dimensional, finite-element model constrained by the geological relations in the Notch Peak aureole, Utah. Results show that CO₂ strongly affects fluid-flow patterns in contact aureoles. Infiltration of magmatic water into a homogeneous aureole containing CO₂–H₂O sedimentary fluid facilitates upward, thermally driven flow in the inner aureole and causes downward flow of the relatively dense CO₂-poor fluid in the outer aureole. Metamorphic CO₂-rich fluid tends to promote upward flow in the inner aureole and the progress of devolatilization reactions causes local fluid expulsion at reacting fronts. We also tracked the temporal evolution of P-T-X\textsubscript{CO₂} conditions of calc-silicate reactions. The progress of low- to medium-grade (phlogopite- to diopside-forming) reactions is mainly driven by heat as the CO₂ concentration and fluid pressure and temperature increase simultaneously. In contrast, the progress of the high-grade wollastonite-forming reaction is mainly driven by infiltration of chemically out-of-equilibrium, CO₂-poor fluid during late-stage heating and early cooling of the inner aureole and thus it is significantly enhanced when magmatic water is involved. CO₂-rich fluid dominates in the inner aureole during early heating, whereas CO₂-poor fluid prevails at or after peak temperature is reached. Low-grade metamorphic rocks are predicted to record the presence of CO₂-rich fluid, and high-grade rocks reflect the presence of CO₂-poor fluid, consistent with geological observations in many calc-silicate aureoles. The distribution of mineral assemblages predicted by our model matches those observed in the Notch Peak aureole.

Key words: contact aureoles; CO₂–H₂O fluid; mineral reactions; P-T-X path; reactive flow.

INTRODUCTION

Fluid flow plays important roles in various geological processes by affecting mechanical properties of crustal rocks (Etheridge & Wall, 1983; Lister, 1977; Marsh, 1989; McTigue, 1987) and by contributing to heat and mass transport (Ferry, 1994; Hanson, 1995; Knapp & Knight, 1977). Numerous studies have investigated the dynamics of fluid flow during contact metamorphism using numerical simulations (Cartwright & Weaver, 1997; Cook & Bowman, 1997; Cui et al., 2001, 2002; Hanson, 1995; Hayba & Ingebritsen, 1997; Norton & Knight, 1977). Our two-dimensional (2-D) simulations of fluid flow in contact metamorphic aureoles with layered permeability structures (Cui et al., 2001, 2002) have shown strong time- and space-dependence of fluid flow, which may strongly influence the redistribution of oxygen isotopes and the thermal evolution of aureoles. Because various assumptions were made in these numerical models for tractability, many important aspects of fluid flow have not been sufficiently explored. Foremost was the assumption of a pure H₂O fluid. CO₂ and other species are common fluid components in contact metamorphic aureoles and other crustal systems, including metamorphic terranes, geothermal systems, and ore deposits (e.g. Kerrick, 1974; Takenouchi & Kennedy, 1964).

In calc-silicate contact aureoles, CO₂ is produced by decarbonation mineral reactions (e.g. Ferry, 1996; Kerrick, 1974; Nabelek et al., 1984). Experimental and theoretical studies have shown that the thermodynamic and physical properties of the CO₂–H₂O system are quite different from those of pure water (e.g. Blencoe et al., 2001; Duan et al., 1992; Frost & Wood, 1997; Sterner & Bodnar, 1991; Takenouchi & Kennedy, 1964). Thus, the dynamics of a mixed CO₂–H₂O fluid flow during metamorphism is likely to differ from the flow of a pure H₂O fluid.

Evidence indicates significant influence of CO₂ and other chemical species on metamorphism. The progress of decarbonation reactions can be driven either...
by heat or by chemically disequilibrium fluid (e.g. Walther, 1996). Reactions driven by water-rich fluids have been documented in many calc-silicate aureoles (e.g. Davis & Ferry, 1993; Ferry, 1989, 1996; Ferry et al., 1998; Nabelek et al., 1984). For example, water-rich fluid was shown by mineral equilibria (e.g. Labotka et al., 1988; Nabelek & Labotka, 1993) and fluid inclusions (Novick & Labotka, 1990) to have existed in the wollastonite zone of the Notch Peak aureole, Utah, although the source of water-rich fluid in the aureole has been debated (e.g. Ferry & Dipple, 1992; Labotka et al., 1988; Nabelek & Labotka, 1993). A water-rich fluid can be magmatic water from a nearby crystallizing pluton, sedimentary pore fluid, or metamorphic water produced by dehydration reactions. Sedimentary pore fluid tends to develop thermally driven circulation, whereas the release of magmatic water promotes radial down-temperature flow, particularly during early metamorphic stages (Cui et al., 2001; Hanson, 1995). The thermodynamics of each specific fluid may have different impacts on mineral reactions, consequently resulting in characteristic distributions of mineral assemblages in contact aureoles (Ferry & Dipple, 1991, 1992). Furthermore, the progress of a decarbonation reaction can be strongly influenced by the dynamics of CO₂ transport away from the reaction front.

In this work we investigated the coupled, aureole-scale flow of reactive CO₂–H₂O fluid with the progress of calc-silicate reactions. A 2-D finite-element model was built that solves equations for combined heat transport, fluid flow, and kinetics of mineral reactions. With geological constraints from the Notch Peak aureole, Utah, we systematically investigated the flow of mixed CO₂–H₂O fluid and transport of CO₂ and its impact on the progress of calc-silicate reactions.

GEOLOGY OF THE NOTCH PEAK AUREOLE

The Notch Peak contact metamorphic aureole in the House Range, west-central Utah, resulted from intrusion of the Jurassic granitic Notch Peak stock into a sequence of Cambrian formations (Fig. 1). The intrusion occurred at 4–5 km depth and the pluton has a columnar shape with an estimated radius of at least 4 km in the subsurface (Nabelek et al., 1986). The roof of the intrusion consists of the Orr Formation, a sequence of interbedded nearly pure limestones and calcareous argillites (Fig. 2). Below the Orr Formation is the 360-m-thick Weeks Formation, which is a relatively thinly bedded siliceous limestone with abundant graphite in the bottom approximately 125 m. The underlying Marjum Formation is similar to the Weeks Formation. Below the Marjum Formation is a sequence of interbedded Middle to Lower Cambrian massive limestones and shales. The unexposed lowest part of the aureole is probably the >1500-m-thick Prospect Mountain Quartzite (Hintze, 1974).

Previous studies of the aureole focused on two upper sedimentary units, the 220-m-thick Big Horse Member of the Orr Formation and the underlying Weeks Formation (Hover-Granath et al., 1983; Labotka et al., 1988; Nabelek, 2002; Nabelek & Labotka, 1993; Nabelek et al., 1984, 1986, 1992; Novick & Labotka, 1990). Metamorphic reactions in the marble layers of the Big Horse Member occurred in equilibrium with a CO₂-rich fluid phase at all grades, resulting in forsterite + tremolite + dolomite + calcite-bearing assemblages at the highest grade (Hover-Granath et al., 1983).

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Fig. 1. Simplified geological map of the Notch Peak contact metamorphic aureole, Utah (after Hintze, 1974; Nabelek & Labotka, 1993). The heavy lines show metamorphic isograd as defined by mineral assemblages in calcareous argillites. The heavy dashed line marks the position of a pre-intrusion fault.

Fig. 2. Stratigraphy of the Notch Peak aureole (after Hintze, 1974).
Sedimentary rocks in the Big Horse Member and the Weeks Formation. Values for different metamorphic zones in both units are shown.

Because the assemblages within the marbles are mostly univariant, Hover-Granath et al. (1983) argued that fluids within the marbles were internally buffered and therefore the layers were closed to influx of external fluids. The marble layers have uniform sedimentary δ¹⁸O and δ¹³C values of about 20.5‰ and 0.5‰, respectively, at all grades (Fig. 3), underscoring the impermeability of the marbles to external fluids during the metamorphic event (Hover-Granath et al., 1983; Nabelek et al., 1984).

In contrast, metamorphic reactions in all calcareous argillite units occurred in the presence of progressively more H₂O-rich fluid as metamorphic grade increased (Hover-Granath et al., 1983; Labotka et al., 1988; Nabelek et al., 1992). The unmetamorphosed argillites consist of calcite (Cal), dolomite (Dol), quartz (Qtz), and muscovite (Ms). The lowest metamorphic grade is defined by the wollastonite-forming (Wo) reaction

$$\text{Wo} + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$$

Any wollastonite-grade rocks also contain vesuvianite and have δ¹⁸O values down to 9.5‰, approximately the value of the stock. Because reactions that formed the highest-grade rocks were mostly decarbonation reactions, the low fluid XCO₂, and rock δ¹⁸O values imply infiltration of an externally derived, water-rich fluid into the wollastonite zone. The estimated radial distances of the isograds from the shallow dipping contacts of the intrusion are about 1300 m for the phlogopite isograd, 700 m for the diopside isograd, and 350 m for the wollastonite isograd (Nabelek & Labotka, 1993) (Fig. 1). The calc-silicate reactions caused up to 30% volume loss of the initial rocks (Labotka et al., 1988; Nabelek & Labotka, 1993).

**Numerical Model**

**Governing equations**

As in previous hydrodynamic studies (e.g. Cook & Bowman, 1997; Cui et al., 2001; Gerdes et al., 1998; Hanson, 1995; Norton & Taylor, 1979), it was assumed that fluid flow in contact aureoles follows Darcy’s law:

$$v = -\left(\frac{K}{\mu}\right)\nabla P$$

where v is the seepage velocity for fluid flowing through a porous medium, K is the intrinsic permeability tensor, \(\mu\) is viscosity of the fluid, \(\rho\) is fluid density as a function of fluid pressure, temperature, and chemical composition, and \(g\) is the gravitational acceleration. In an isotropic medium, the permeability tensor can be reduced to a scalar as was done in this study. Constant values of model parameters are listed in Table 1, and variables are described as needed.

The conservation equation for fluid mass, coupled with Darcy’s law (1) and expressed in terms of primary variables pressure (\(P\)), temperature (\(T\)), and solute concentration (\(C\)), takes the form

$$\frac{\partial p}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = -\nabla \cdot (\rho \mathbf{g})$$

where \(t\) is time, \(Q\) represents fluid sources or sinks, including water released from a crystallizing magma and metamorphic fluid produced by devolatilization reactions. Here, a constant porosity was assumed and thus instantaneous compaction of rock matrix as in previous studies (e.g. Ague & Rye, 1999; Hanson, 1995). The deformation of rocks caused by the progress of reactions was also neglected because ductile deformations in the Notch Peak aureole were observed only in few calc-silicate laminae near the pluton. The fluid was assumed to be mixed CO₂–H₂O fluid. The thermodynamic properties of CO₂–H₂O mixture under conditions of contact metamorphism are known (e.g. Bottigia & Richet, 1981; Duan et al., 1992; Haar et al., 1984; Holland & Powell, 1991; Schubert & Straus, 1981; Takenouchi & Kennedy, 1964). The compensated Redlich–Kwong (CORK) state equation of Holland & Powell (1991) was used, which is internally consistent with their thermodynamic database for minerals (Holland & Powell, 1998). Although fluid flow in contact aureoles may be potentially multiphase, we chose to focus on one-phase flow for simplicity and because it was likely the prevalent mode of fluid flow in the North Peak aureole (Labotka et al., 1988; Novick & Labotka, 1990).

Heat transport in contact aureoles, including both advection and conduction, takes the form

$$[\phi \rho_c c_p (1 - \phi) + \rho_e c_e] \frac{\partial T}{\partial t} = -\nabla \cdot (k \nabla T) + \nabla \cdot ([\rho c_p (1 - \phi) \mathbf{v} + \rho c_e \mathbf{D}] + H)$$

where \(c_p\) and \(c_e\) are the specific heat of the fluid and the solid grains, respectively; \(\mathbf{v}\) and \(\mathbf{D}\) are the thermal conductivities of the fluid and solid grains, respectively; \(I\) is the identity tensor, and \(H\) is the latent heat consumed by metamorphic reactions or produced by crystallization of the magma. \(\mathbf{D}\) is the hydrodynamic dispersion tensor.
Table 1. List of symbols.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition, values, and units</th>
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<tbody>
<tr>
<td>$c_v$</td>
<td>specific heat of fluid in J kg$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$c_p$</td>
<td>specific heat of solid matrix in J kg$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$f$</td>
<td>fugacity of fluid phases</td>
</tr>
<tr>
<td>$g$</td>
<td>gravitational acceleration vector (9.8 m s$^{-2}$)</td>
</tr>
<tr>
<td>$i$</td>
<td>subscript represents mineral phases</td>
</tr>
<tr>
<td>$j$</td>
<td>subscript represents mineral reactions</td>
</tr>
<tr>
<td>$k^p$</td>
<td>intrinsic reaction rate constant $\left(5.0 \times 10^{-14} \text{ kmol m}^{-2} \text{s}^{-1} \cdot \text{kmol}^{-1} \text{mol}^{-1} \right)$</td>
</tr>
<tr>
<td>$m$</td>
<td>mineral abundance in kmol-m$^{-3}$</td>
</tr>
<tr>
<td>$n$</td>
<td>reaction order (assumed to be 1 in this study)</td>
</tr>
<tr>
<td>$s$</td>
<td>time in second(s)</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>average seepage velocity of fluid flow in m s$^{-1}$</td>
</tr>
<tr>
<td>$A$</td>
<td>reacting surface area of controlling minerals in m$^2$ m$^{-3}$</td>
</tr>
<tr>
<td>$E_a$</td>
<td>reaction activation energy $\left(8.5 \times 10^8 \text{ kJ mol}^{-1} \right)$</td>
</tr>
<tr>
<td>$C$</td>
<td>CO$_2$ concentration of fluid (mole fraction)</td>
</tr>
<tr>
<td>$C^*$</td>
<td>CO$_2$ concentration of fluid sources or sinks (mole fraction)</td>
</tr>
<tr>
<td>$D$</td>
<td>molecular diffusivity of CO$_2$ in fluids (1.0 $\times$ 10$^{-9}$ m$^2$ s$^{-1}$)</td>
</tr>
<tr>
<td>$D_t$</td>
<td>dispersion tensor in m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$H$</td>
<td>latent heat of sources or sinks in J m$^{-3}$ s$^{-1}$</td>
</tr>
<tr>
<td>$I$</td>
<td>identity tensor $\left(2 \times 2 \right)$</td>
</tr>
<tr>
<td>$K$</td>
<td>intrinsic permeability tensor in m$^2$</td>
</tr>
<tr>
<td>$M$</td>
<td>mole mass of phases (kg kmol$^{-1}$)</td>
</tr>
<tr>
<td>$P$</td>
<td>fluid pressure in Pa</td>
</tr>
<tr>
<td>$Q$</td>
<td>fluid mass sources or sinks in kg m$^{-3}$ s$^{-1}$ or kmol m$^{-3}$ s$^{-1}$</td>
</tr>
<tr>
<td>$R$</td>
<td>universal gas constant (8.3144 kJ kmol$^{-1}$ K$^{-1}$)</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature in °C or K</td>
</tr>
<tr>
<td>$T^*$</td>
<td>reference temperature in °C (743 K)</td>
</tr>
<tr>
<td>$\mu$</td>
<td>fluid dynamic viscosity in Pa s</td>
</tr>
<tr>
<td>$P_f$, $\rho_f$, $\phi$</td>
<td>densities of fluid (kg m$^{-3}$ or kmol m$^{-3}$) and solid grains (2750.0 kg m$^{-3}$)</td>
</tr>
<tr>
<td>$\phi$</td>
<td>effective porosity</td>
</tr>
<tr>
<td>$q$</td>
<td>fluid source component ($\sigma$)</td>
</tr>
<tr>
<td>$\Delta g_i$</td>
<td>symbol definition, values, and units</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>reaction enthalpy change in kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$\Delta S$</td>
<td>reaction entropy change in kJ mol$^{-1}$ K$^{-1}$</td>
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(2 x 2) and is determined by the fluid velocity ($\mathbf{v}$), and the longitudinal ($\alpha_{L}$) and the transverse ($\alpha_{T}$) dispersivities (cf. Voss, 1984).

Hydrodynamic dispersion in contact aureoles is common because of the intrinsic heterogeneity of hydrologic properties of lithologies and geological structures on all scales. A critical review of experimental data on hydrodynamic dispersion in the field has been given by Gelhar et al. (1992). In this study, conservative values of $x_L = 200$ m and $x_T = 50$ m were used, which are within the range of experimental data (Gelhar et al., 1992).

Conservation of the mass of CO$_2$ in the CO$_2$–H$_2$O fluid is expressed as

$$\frac{\partial C}{\partial t} = -\nabla \cdot \mathbf{v} + \nabla \cdot (|\phi_f| \mathbf{Df} + D \nabla C) + Q(C - C^*),$$

where $C$ is the concentration of CO$_2$ in fluid, which is treated as the mole fraction of CO$_2$. Consequently, the fluid density ($\rho_f$) in equation 4 has units of kmol-m$^{-3}$, and fluid source ($Q$) has units of kmol-m$^{-3}$ s$^{-1}$. Therefore, $C$ is interchangeable with $X_{CO_2}$, which is usually used in the petrological literature. $C$ is CO$_2$ concentration in the fluid source, and $D$ is the apparent molecular diffusivity of CO$_2$ in the mixed fluid. The diffusion through minerals is neglected because it is slow compared to the evolution of contact aureoles.

The mineral reaction system in rocks is given by

$$\sum_i \gamma_i \phi_i = 0,$$

where $\phi_i$ represents a mineral $i$ or a component in fluid phase (i.e. CO$_2$ or H$_2$O). $\gamma_i$ is the stoichiometric coefficient for phase $i$ in $j$th mineral reaction; the stoichiometric coefficients are negative for reactants and positive for products. The net production or consumption rate of a mineral $i$ within a unit volume of rock is determined by summing up the production of reaction rate $r_j$ and stoichiometric coefficient $\gamma_i$ over all reactions. Therefore, the net change in the mass of mineral $i$ due to all reactions is given by

$$\frac{\partial n_i}{\partial t} = \sum_j r_j / \gamma_i.$$
Although a simultaneous solution of all the equations, referred to as the one-step or global implicit method, is conceptually the most straightforward approach, it is computationally inefficient when reactions are coupled with transport processes (Oran & Boris, 1987; Steefel & Lichtner, 1994; Steefel & MacQuarrie, 1996). A more efficient approach is to use an operator- or time-splitting technique to decouple the transport and reaction terms. The techniques include the sequential noniterative approach (SNIA), the Strang splitting approach, and the sequential iteration approach (SIA). The advantages and disadvantages of these solution techniques have been previously discussed (Steefel & MacQuarrie, 1996; Strang, 1968; Valocchi & Malmstead, 1992; Yeh & Tripathi, 1989; Zysset et al., 1994). Recognizing the uncertainties inherent in the metamorphic reactive transport governing equations, in this study we applied the SNIA scheme, which can be easily implemented and is time-efficient. The disadvantage is a higher chance of numerical errors. However, the errors introduced by the operator splitting scheme are insignificant relative to those associated with uncertainties of model parameters and other inherent numerical errors, such as numerical dispersion (Steefel & MacQuarrie, 1996).

The numerical model was developed based on the publicly available SUTRA code (Voss, 1984) with numerous modifications. In the sequential noniteration approach, a single time-step consists of a transport step that is followed by a reaction step. In the transport step, heat, fluid and solute mass conservation eqns 2, 3, 4 were solved without heat and mass sources contributed by mineral reactions. In the reaction step, with the newly obtained $P$, $T$ and $C$, the following equations:

\[ \frac{\partial P}{\partial t} + \nabla \cdot (P \mathbf{V}) = Q, \]

\[ \frac{\partial T}{\partial t} + \nabla \cdot (T \mathbf{V}) = Q_h, \]

\[ \frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial x^2}, \]

\[ \frac{\partial P}{\partial t} + \nabla \cdot (P \mathbf{V}) = Q_h(C - C_0), \]

(12)

(13)

(14)

(together with eq. 6) were solved within the same time step using the well-developed subroutine ODE that implements the variable-step, variable-order Adams method (Shampine & Gordon, 1975). The solutions from the reaction step were then used to get the new transport solutions in the next time step.

The implementation scheme outlined above is only necessary for cases that simulate coupled fluid flow with progress of mineral reactions. When the progress of mineral reaction was considered to be solely a function of temperature (Cui et al., 2001) or when no mineral reactions were considered, the transport of CO$_2$ was modelled by solving equations 1–4 using the one-step global implicit method. Throughout the computations, the solutions for temperature, fluid pressure, and CO$_2$ concentration ($\chi_{CO_2}$) converged to $1.0 \times 10^{-2}$ °C, $1.0 \times 10^5$ Pascal, and $1.0 \times 10^{-2}$, respectively, at each time step. Variable time-step sizes were calculated with the maximal Darcy’s velocity from previous time step in a way so that the fluid could move no more than the half-length of each element with a uniform grid size of $200 \times 200$ m.

Physical properties of the model

The model is constrained by the geology of the Notch Peak aureole. Most physical properties of the model were discussed in our previous work (Cui et al., 2001, 2002). The size of the model pluton (Fig. 4) approximates the estimated dimensions of the columnar Notch Peak intrusion. Only half of the pluton is shown because of the symmetry. Only depths > 3 km below the surface were considered in the model for two reasons. First, metamorphism only occurred in formations near the pluton, including the Big Horse Member and Weeks Formation. Second, the assumption of one-phase, mixed CO$_2$–H$_2$O fluid most likely holds at these depths.

Previous studies (e.g. Hover-Granath et al., 1983; Nabelek et al., 1984) indicated that a large amount of CO$_2$-poor magmatic fluid infiltrated into calc-silicate rocks such as the Weeks Formation, whereas virtually no fluid penetrated into pure limestone beds like those in the Big Horse Member of the Orr Formation. This resulted in extensive $^{18}$O exchange in calc-silicate rocks, whereas the protolith $\delta^{18}$O values in pure limestone/marble layers were preserved. In an analogous isotopic work, Hoernes & Voll (1991) have shown no fluid infiltration into quartzite in the Ballachulish aureole, Scotland. Therefore, in our models with layered permeability structures, calc-silicate layers were considered as aquifers and pure limestone and quartzite layers as aquitards, as shown in Fig. 4. However, the permeability structure approximates only an averaged distribution of lithologies in the aureole due to the coarse mesh used here. The applied permeability values are within the range of experimental and theoretical values (Brace, 1984; Hanson, 1995; Manning & Ingebritsen, 1999) and are confirmed by measurements on the Notch Peak rocks (Cui et al., 2001). The effective porosity was determined from the specified permeability by a cubic law relationship (Cui et al., 2001; Walsh & Brace, 1984), with an effective reference porosity of 0.01 at a permeability value of $1.0 \times 10^{-16}$ m$^2$.

For most cases, the upper boundary of the model domain was assumed to be permeable with constant fluid pressure (500 bar), temperature (100 °C), and $\chi_{CO_2}$. The bottom boundary is impermeable with a fixed temperature of 225 °C. The left edge of the model domain is a symmetrical boundary, i.e. no heat and mass flux crosses it. The right edge was assumed to be permeable with a hydrostatic pressure gradient, a vertical thermal gradient of 25 °C km$^{-1}$, and a constant $\chi_{CO_2}$. We also tested different boundary conditions, including an impermeable right edge and conductive heat flux at the bottom of the model domain in selected cases. However, the results from these cases do not change appreciably.

The granitic pluton was assumed to have been emplaced instantaneously with a uniform temperature of 900 °C. The wall-rock domain has a metamorphic geothermal gradient of 25 °C km$^{-1}$. The initial pore fluid was assumed to have a constant CO$_2$ concentration and be thermally equilibrated with the wall rocks. Hydrostatic fluid pressure was therefore applied to the whole model domain according to the specified T-$\chi_{CO_2}$ conditions. The initial pore fluid in the pluton domain was assumed to be pure water. When magmatic fluid production was included, it was assumed that the magma contained...
3 wt% of H2O, which exsolved linearly as temperature decreased from 900 to 750 °C during crystallization.

The latent heat generated by the crystallization of magma or consumed by metamorphic reactions is accounted for by an adjustment of the specific heat of the pluton and the wall rocks (Cui et al., 2001). However, when progress of mineral reactions was considered, the latent heat of reactions was determined by eq. 11. In all cases, viscosity of the CO2–H2O fluid was determined by

\[ \eta = \eta_c + (1 - \eta_c) \eta_w \]

where \( \eta_c \) is the viscosity of CO2 (interpolated from the table of Vesovic et al., 1990), and \( \eta_w \) is the viscosity of water given by Haar et al. (1984).

### NUMERICAL RESULTS

A series of numerical experiments was run to explore the dynamics of heat flow, flow of mixed CO2–H2O fluid, and progress of calc-silicate mineral reactions. Major parameters used in each case are listed in Table 2. Cases 1 and 2 show the influence of CO2 on the fluid flow pattern. The effects of CO2-rich metamorphic fluid released as a linear function of temperature were investigated in cases 3 and 4. Cases 5–7 show the results of coupling mineral reactions with the flow of CO2-bearing fluids and its effects on the metamorphic reaction paths.

### Influence of CO2 on fluid-flow field

Figure 5 shows interactions between magmatic water and CO2-containing pore fluid without mineral reactions (case 1; Table 2). Early in the evolution of the aureole (< 1000 years), the release of magmatic water, which is assumed to be pure water, drives radial flow away from the pluton in the whole aureole and dilutes CO2 near the pluton (Fig. 5a). By 10 000 years, low-CO2 fluids dominate the inner aureole and a vigorous convection cell develops near the pluton (Fig. 5b). At the right edge of the pluton, fluid flows upward, driven mainly by thermal buoyancy. At 2–3 km from the pluton, relatively CO2-poor fluid flows downward along a zone of sharp XCO2 gradients because the CO2-poor fluid is denser than a CO2-rich fluid.
fluid at the model $P$–$T$ conditions. By 30 000 years, the CO$_2$-containing fluid from the country rocks flows toward the pluton, confining the circulation cell of the CO$_2$-poor fluid to the inner aureole (Fig. 5c). Horizontal inward flow along the bottom of the model domain enriches CO$_2$ in the aureole. At all times during the metamorphism, a strong upward flow along the right edge of the pluton is predicted.

The dramatic effects of dissolved CO$_2$ on the flow pattern become more evident in comparison with that of a pure-H$_2$O pore fluid (case 2; Fig. 6). Although the early radial flow caused by release of magmatic water is similar in both cases, the strong downward flow (Fig. 5b) is missing for the pure-H$_2$O pore fluid (Fig. 6). In the outer aureole, dispersed inward flow in Fig. 6 is in contrast to the outward flow of CO$_2$-poor fluid in Fig. 5(b). This flow pattern remains up to 30 000 years with slightly decreasing magnitude of fluid-flux.

**Effects of metamorphic CO$_2$–H$_2$O fluid**

The major source of CO$_2$ in calc-silicate contact aureoles is from decarbonation reactions. For the purpose of illustration, it was assumed that the CO$_2$-rich metamorphic fluid with a $X_{CO_2}$ value of 0.8 was released linearly between 300 and 600 °C to a maximum value of 10 wt% of the wall rocks. In case 3 with homogeneous permeability, the metamorphic fluid was assumed to be released from both calc-silicate and limestone layers (Fig. 4). The effects of layered permeability were considered in case 4, in which metamorphic fluid was released only from calc-silicate layers. Both cases 3 and 4 also include the release of 3 wt% magmatic water.

In an aureole with a homogeneous wall-rock permeability (case 3; Table 2), the released metamorphic fluid can raise $X_{CO_2}$ up to 0.4 above the pluton and near its upper right corner and causes strong upward flow during the first several thousands of years (Fig. 7a). Release of magmatic water also develops a component of radial flow and significantly reduces CO$_2$ concentration below the pluton. By 10 000 years, most metamorphic CO$_2$ has been advected away from the aureole by magmatic water and/or sedimentary fluid flow (Fig. 7b). The major flow features include vigorous vertical flow above and along the right edge of the pluton and dispersive inward flow of sedimentary fluid in the lower part of the aureole. The flow pattern at this stage is similar to the pure-water case (Fig. 6) and contrasts with the vigorous circulation of the CO$_2$-poor fluid in case 1 that does not include metamorphic fluid (Fig. 5b). By 30 000 years, fluid-flow becomes dominated by sedimentary fluid in the whole aureole (Fig. 7c).

Case 4 (Table 2) features release of magmatic water and metamorphic fluid into layered wall rocks (Fig. 4). The results show strong horizontal flow in aquifers (Fig. 8a). However, the one-order magnitude difference of permeability between the aquifers and the aquitards does not prevent vertical flow above the pluton (Fig. 8a). A high $X_{CO_2}$ value of about 0.4 is limited to the zones right above the pluton. By 10 000 years, in most of the inner aureole the CO$_2$ is diluted by magmatic water, and the outward flow wanes (Fig. 8b). By 30 000 years, fluid flow becomes horizontally up-temperature in the side aureole, and the whole aureole is dominated by low $X_{CO_2}$ (about 0.05) fluid (Fig. 8c).

Without magmatic water, release of metamorphic fluids can raise $X_{CO_2}$ up to 0.8 along the upper margins of the pluton in both homogeneous and layered aureoles, although the flow pattern remains similar except for a shorter duration of early radial flow. However, the reaction-produced CO$_2$ can still be diluted promptly out of inner aureole by circulation of CO$_2$-poor sedimentary fluid.

These simulations show that CO$_2$-rich metamorphic fluid causes early CO$_2$ enrichment in the inner aureole and enhances upward flow above the pluton. However, most CO$_2$-rich fluids are advected away by magmatic water and/or sedimentary fluid flow in a few thousand years after emplacement of the pluton.

**Calc-silicate reactions and distribution of minerals**

In the preceding section we highlighted the influence of CO$_2$-rich metamorphic fluids on flow patterns in calc-silicate contact aureoles by assuming a linear release of the fluids with temperature. However, in nature, the release of metamorphic fluids is controlled by the progress of mineral reactions. The progress of each mineral reaction is a kinetic process defined by the rates of heat input and flow of a chemically disequilibrium fluid. Other possible rate-limiting processes include dissolution and growth of
minerals and mass-transfer into or out of the reacting sites. These processes are individually poorly constrained but are approximated within the intrinsic reaction-rate constant \( k_0 \) in eq. 9.

In this section the results of simulations of the coupled fluid flow and the progress of calc-silicate reactions are shown. The model mineral reactions are listed in Table 3; Fig. 9 shows their phase relationship at a fluid pressure of 750 bar. The reaction system
Table 3. Model mineral reactions. The occurrences of reactions 3–8 in the Notch Peak aureole are indicated by observations. However, reactions 1–2 are also included, although there is no evidence for their occurrence in the Weeks Formation. The minerals in bold were assumed to be the controlling minerals of their corresponding reactions because they have the lowest abundances.

<table>
<thead>
<tr>
<th>Reaction #</th>
<th>Reaction</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>3 Dol + 4 Qtz + 1 H2O = 3 Cal + 1 Tlc + 3 CO2</td>
</tr>
<tr>
<td>2</td>
<td>6 Cal + 4 Qtz + 5 Tk = 3 Tr + 6 CO2 + 2 H2O</td>
</tr>
<tr>
<td>3</td>
<td>5 Dol + 8 Qtz + 1 H2O = 3 Cal + 1 Tr + 7 CO2</td>
</tr>
<tr>
<td>4</td>
<td>3 Dol + 2 Qtz + 1 Ms = 2 Cal + 1 An + 1 Phil + 4 CO2</td>
</tr>
<tr>
<td>5</td>
<td>1 Cal + 2 Qtz + 1 Ms = 1 Mc + 1 An + 1 CO2 + 1 H2O</td>
</tr>
<tr>
<td>6</td>
<td>6 Cal + 24 Qtz + 5 Phil = 3 Tr + 5 Mc + 6 CO2 + 2 H2O</td>
</tr>
<tr>
<td>7</td>
<td>3 Cal + 2 O2 + 1 Tr + 5 Di + 3 CO2 + 1 H2O</td>
</tr>
<tr>
<td>8</td>
<td>1 Cal + 1 Qtz = 1 Wo + 1 CO2</td>
</tr>
</tbody>
</table>

Fig. 9. T–XCO2 diagram of major calc-silicate mineral reactions in the Notch Peak aureole at 750 bar (Table 3). Phase boundaries were determined with THERMOCALC 2.7 (Powell & Holland, 1988).

approximates the calc-silicate reactions in the Notch Peak aureole (Hover-Granath et al., 1983; Labotka et al., 1988; Nabelek, 2002; Nabelek & Labotka, 1993). Although there is no evidence for the occurrence of talc (Tlc) in the Weeks Formation because of the rocks’ fairly Fe-rich composition (Nabelek, 2002), an assemblage Cal + Tlc + Tr + Dol occurs in the more magnesian limestone layers of the Big Horse Member (Hover-Granath et al., 1983). Therefore, the related reactions (1 & 2) are also included in the model system.

The reaction system in our model behaves more like an open system and thus both heat and fluid that is out of chemical equilibrium with an infiltrated rock can contribute to the progress of an endothermic decarbonation reaction. However, one of the parameters will likely predominate. The terms ‘heat-driven’ or ‘fluid-driven’ are used to refer to the dominant parameter. To determine quantitatively the proportion of each parameter in driving a reaction requires a large amount of computation that slows processing time. However, a reaction can be described as either ‘heat-driven’ or ‘fluid-driven’ qualitatively based on its characteristic P-T-X path. A reaction is defined as ‘heat-driven’ if its progress is accompanied by a simultaneous increase in temperature, XCO2, and fluid pressure. The simultaneous increase indicates that infiltration of a disequilibrium CO2-poor fluid into the reaction front is at a low rate, if any. Moreover, increasing pressure makes it rather difficult for an external fluid to infiltrate into the reaction front, instead it causes fluid expulsion. Therefore, it is appropriate to call such a reaction ‘heat-driven’ even if some heat may be advected to the reaction site by the fluid. A reaction is called ‘fluid-driven’ if the reaction progress is accompanied by little increase or even a decrease in temperature while XCO2 decreases due to the high rate of fluid infiltration compared to the rate of heat supply. Although a pressure drop could also drive the progress of a decarbonation reaction, XCO2 will increase if aqueous fluid does not play a major role. Therefore, it is also appropriate to refer a reaction ‘fluid-driven’ if its progress is accompanied by decreases of XCO2 and temperature and even a decrease in pressure.

For cases with homogeneous permeability, the wall rocks were assumed to initially consist of dolomite, quartz, calcite, and muscovite, and their abundances are 1.48, 7.13, 19.4, and 0.227 kmol-m⁻³, respectively. The abundances approximate those in the unmetamorphosed calc-silicates in the Weeks Formation in the Notch Peak aureole (Nabelek et al., 1992). The bottom quartzite layer shown in Fig. 4 consists of only quartz. In models with a layered permeability structure, all aquifer layers have the same initial mineral assemblage as the homogeneous wall rocks. However, because the aquitards were assumed to consist of only calcite or quartz, no reactions occur in them. For simplicity and generality, conservatively rapid reaction-rate constants were adopted in the governing equations for the progress of all mineral reactions (Table 1). Recognizing the uncertainties in nucleation, reaction-rate constants, and other thermodynamic parameters, it was assumed that the minerals have a constant spherical shape with a radius of 1.0 mm, although in detail the grain sizes must change with time (Águ & Rye, 1999). The reactive surface area (A) of the controlling mineral in each reaction is determined accordingly.

Figure 10 shows the predicted XCO2 and temperature fields in a layered-permeability aureole with progress of mineral reactions (case 5; Table 2). By 1000 years, high-XCO2 fluid is produced by the devolatilization reactions near the margins of the pluton, but the fluid is partly flushed away from the reacting zones by the magmatic water (Fig. 10a). By 10 000 years, the magnitude of XCO2 values decreases significantly to about 0.2 in the upper inner aureole (Fig. 10b). By 30 000 years (Fig. 10c), the XCO2 of the fluid in the aureole is mostly reduced back to the initial value (0.01) except for fluid directly above the pluton. The
The general trend of changing fluid composition is similar to that in cases of linear release of metamorphic fluid with temperature (Fig. 8), but in this case more diluted metamorphic fluid remains in the aureole at 30 000 years.

The release of metamorphic fluid during mineral reactions raises fluid pressure, and results in expulsion of the fluid from the reaction sites (Fig. 11). The background, low-magnitude fluid flux evolves gradually, similarly to previous cases. During early stages, the release of magmatic water and metamorphic fluid causes outward, down-temperature and focused flow within aquifers (Fig. 11a). By 10 000 years, the background flow switches to inward, horizontal flow in the

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**Fig. 10.** Snapshots of predicted thermal and $X_{\text{CO}_2}$ fields in case 5 (Table 2; legend as Fig. 5). (a) CO$_2$-rich metamorphic fluid released by mineral reactions in aquifers concentrates near the pluton at 1000 years, (b) and (c) metamorphic CO$_2$ is diluted out of inner aureole at later stages by magmatic water and/or sedimentary fluid, similar to the CO$_2$ evolution trend in case 4 (Fig. 8).

**Fig. 11.** Snapshots of predicted fluid flow and pressure fields in case 5 (Table 2) at 1000 years (a), 10 000 years (b), and 30 000 years (c). The arrows are fluid mass flux vectors as defined in Fig. 5. Thick arrows and fine arrows are scaled by the thick arrow and the fine one at top of each snapshot, respectively, to highlight flux at reaction fronts and rest nonreacting area. The grey lines are contours for fluid pressure. Note that only part of the model domain is shown. Release of metamorphic fluid by progressing mineral reactions results in enhanced fluid flux, elevated fluid pressures, and local fluid expulsions at reaction fronts.
aquifers (Fig. 11b); the flow pattern remains that way at 30 000 years (Fig. 11c).

Metamorphic $P-T-X_{CO_2}$ paths of the fluid-rock system in the side aureole (locations 1 & 2 in Fig. 4) are shown in Fig. 12. At location 1, which is 200 m distant from the right edge of the pluton, the rock experiences rapid heating and a slight reduction of $X_{CO_2}$ in the first 100 years due to the infiltration of magmatic water from the pluton (Fig. 12a). Then by about 900 years, $X_{CO_2}$ increases to $> 0.5$ with the progress of low-grade devolatilization reactions. The $T-X_{CO_2}$ trajectory follows approximately the phase boundaries of the low-grade mineral reactions. The simultaneous increases in temperature, fluid pressure, and $X_{CO_2}$ suggest that the progress of the low-grade devolatilization reactions is mainly driven by heat input from the pluton. Thereafter, the rock continues to experience heating but $X_{CO_2}$ drops, possibly due to approach to cessation of low-grade reactions (Figs 12 & 13a). At approximately 1100 years, $X_{CO_2}$ is reduced to about 0.25, fluid pressure drops from around 1300 to 800 bar, while the temperature continues to increase steadily. The diopside-forming reaction begins at approximately 1100 years. It is mainly driven by heat and causes another increase in fluid pressure and $CO_2$ concentration until 1600 years, when the fluid-driven progress of the reaction becomes dominant (Figs 12 & 13a). The wollastonite-forming reaction begins at approximately 2000 years. It is initially driven by heat with increases in fluid pressure and $X_{CO_2}$ for 1000 years (Fig. 12), resulting in growth of about 20% of the total wollastonite in the rock (Fig. 13a). Subsequently, the rock undergoes cooling. However, the wollastonite-forming reaction progresses further with decrease in $X_{CO_2}$ driven by influx of $CO_2$-poor fluid from the pluton and/or the sedimentary rocks until about 17 000 years, when it reaches completion (Figs 12a & 13a).

Rock 2 at 400 m distant from the right edge of the pluton, experiences a different metamorphic history. Prior to 2000 years, the fluid composition is influenced solely by the metamorphic reactions that occur closer to the pluton. Subsequently, the low-grade heat-driven reactions progress with simultaneous increases in temperature, pressure, and $X_{CO_2}$, up to 4300 years when talc begins to disappear (Figs 12 & 13b). Afterwards, $X_{CO_2}$ decreases and fluid pressure drops. From 15 000 to 30 000 years, the $T-X_{CO_2}$ path parallels that of the diopside-forming reaction, but this results from the progress of mineral reactions in the surrounding rocks since no diopside grows in rock 2 (Fig. 13b).

Rock 3 at 200 m above the pluton (Fig. 4) has a similar predicted metamorphic $P-T-X_{CO_2}$ path as rock 1 prior to the onset of the wollastonite-forming reaction at 2000 years (Fig. 14a). Thereafter, however, wollastonite growth is mainly driven by heat up to 8000 years, resulting in about 50% of the total wollastonite in the rock (Figs 14a & 15a), in contrast to only about 20% of heat-driven growth of wollastonite in rock 1 (Fig. 13a). Rock 3 stays near the peak temperature of 540 °C approximately from 7600 to 22 000 years. Rock 4 at 400 m above the pluton begins low-grade reactions at approximately 2500 years, driven by heat with simultaneous increases in $X_{CO_2}$ and fluid pressure. It experiences the mainly heat-driven growth of diopside, but the mainly fluid-driven growth of wollastonite beginning at about 14 000 years (Figs 14a & 15b), in contrast to only heat-driven, low- to medium-grade metamorphism in rock 2 in the side aureole (Fig. 13b).

An interesting feature is that $X_{CO_2}$ and fluid pressure within the metamorphic rocks change synchronously.
Except for first several hundred years, an increase in $X_{CO_2}$ always accompanies an increase in fluid pressure due to the release of CO$_2$-rich fluid by mainly heat-driven reactions, and a decrease in $X_{CO_2}$ accompanies a drop in fluid pressure with waning of the heat-driven progress of reactions (Figs 12–14). Low- to medium-grade reactions are mainly driven by relatively rapid heating with increases in both pressure and $X_{CO_2}$, whereas the high-grade wollastonite-forming reaction is mainly driven by chemically disequilibrium fluid with decrease in $X_{CO_2}$ under relatively low fluid pressure. In rocks near the pluton, model low-grade minerals, including talc, tremolite and phlogopite, grow almost simultaneously in the first 1000 years and then they are consumed by the growth of higher-grade minerals (Figs 13a & 15a). In rocks away from the pluton, mineral growth is temporally more distinct and lower-grade minerals have a longer life span before they are consumed by the growth of higher-grade minerals (Figs 13b & 15b).

The predicted mineral abundances and spatial distributions are shown in Fig. 16. Wollastonite occurs within a 400-m-thick calc-silicate aquifer layer above the pluton, with abundance as high as 3.7 kmol m$^{-3}$. It also occurs within a 200-m-wide zone along the right edge of the pluton. Diopside also occurs in the aquifer above the pluton and in two 400-m-wide zones along the right edge of the pluton, with maximum abundance of 1.5 kmol m$^{-3}$. Anorthite and microcline have almost the same abundance and spatial distributions. Therefore, only anorthite is shown in the figure. It has a similar distribution to diopside, but with abundance of only 0.2 kmol m$^{-3}$. Tremolite and talc occurrences overlap with the outer margins of the diopside zone. Phlogopite only occurs in small patches along the outer side margins of the diopside zones with low abundance of around 0.06 kmol m$^{-3}$. This distribution of the model assemblages generally matches the relation of mineral assemblages in the Notch Peak aureole except for the predicted occurrence of Tlc + Phl + Tr assemblage in the outer aureole (Table 4).

Metamorphic evolution of an aureole with a layered permeability structure but no magmatic water is modelled in case 6 (Table 2; Fig. 17). Without infiltration of magmatic water into the aureole, the maximum $X_{CO_2}$ becomes much higher ($>0.8$) than in case 5.
The cooling of the pluton is slower because less heat is advected out of the pluton. However, the evolution trends of the $X_{\text{CO}_2}$ field and the fluid-flow pattern have very similar features in the two cases. Most metamorphic CO$_2$ is flushed out of the aureole by 30 000 years (Fig. 17c). The flow pattern is dominated by local fluid expulsion at reaction fronts and overall horizontal flow in aquifers, which switches from early stage down-temperature flow to later-stage up-temperature flow by 10 000 years and remains that way thereafter (Fig. 18).

Although the $P$–$T$–$X_{\text{CO}_2}$ paths of rocks in case 6 are similar to case 5, rocks near the pluton experience high $X_{\text{CO}_2}$ of 1.0 at the early stage, in contrast to the lower maximum $X_{\text{CO}_2}$ value of about 0.5 in case 5. The early decrease in $X_{\text{CO}_2}$ and increase in fluid pressure associated with magmatic water in case 5 is absent from case 6. For example, rock 1 experiences only increase in temperature in the first 3000 years (Fig. 19). Then, $X_{\text{CO}_2}$ increases to near 1.0 before 1500 years with progress of mainly heat-driven, low-grade reactions. Thereafter, while maintaining high and slight increase in temperature up to 3000 years, $X_{\text{CO}_2}$ drops from 1.0 to < 0.2 and fluid pressure drops from around 1100 to c. 700 bar with cessation of low-grade reactions (Figs 19 & 20a). The wollastonite-forming reaction in rock 1 starts at about 6000 years, driven by infiltration of the mostly aqueous sedimentary fluid with decreasing temperature and $X_{\text{CO}_2}$, which ends at about 10 000 years, resulting in about 0.2 kmol-m$^{-3}$ wollastonite in the rock (Figs 19a & 20a). Low-grade rocks in case 6 also experience higher $X_{\text{CO}_2}$ than in case 5 at the early stage. For example, influenced by the progress of decarbonation reactions closer to the pluton during the first 3000 years, $X_{\text{CO}_2}$ in rock 2 reaches a maximal value of 0.7, in contrast to about 0.5 in case 5. The talc-forming, heat-driven reaction in rock 2 begins at approximately 3000 years and ceases at about 5000 years. Higher-grade reactions are then driven mainly by aqueous fluid infiltration, together with a slight increase in temperature up to 8000 years (Figs 19 & 20b).

The predicted distribution of minerals is quite similar to case 5. However, because of no infiltration of magmatic water and/or slightly lower peak temperature, case 6 predicts low abundance (< 1.5 kmol-m$^{-3}$) of wollastonite along the right edge of the pluton, in contrast to 3.0 kmol-m$^{-3}$ in case 5 (cf. Figs 16 & 21). In the Notch Peak aureole, talc and tremolite were observed to occur in limestone layers in the Big Horse
Member. However, no talc and only rare tremolite were observed in the Weeks Formation on which the initial mineral abundance of our model mineral system was based. The predicted occurrence of talc and tremolite in cases 5 and 6 is possibly due to the inclusion of talc-forming reactions and low reaction rates in those cases. Therefore, an experiment (case 7) similar to case 5 was conducted, but with the talc-forming reactions 1 and 2 (Table 3) excluded and with the intrinsic reaction rate \( k/\sigma \) increased 20 times. The major features of the flow pattern and the \( X_{\text{CO}_2} \) field are similar to those in case 5. The predicted \( P-T-X_{\text{CO}_2} \) history (Fig. 22) is also similar. Obviously, talc is no longer predicted in the aureole. However, the 20-fold increase in the intrinsic reaction rate still results in the occurrence of tremolite in the aureole, even a higher abundance than in case 5 (Table 4). The abundance of wollastonite is increased by about 30%, but the abundance of phlogopite is reduced. Other low- to medium-grade minerals remain at similar abundances to those in case 5 (Table 4).

When the sedimentary fluid in the aureole has a relatively high \( X_{\text{CO}_2} \) value of 0.1 instead of 0.01, major features of the flow pattern and the predicted metamorphic \( P-T-X_{\text{CO}_2} \) history remain similar to cases 5 and 6. However, when no magmatic water is involved, wollastonite is absent in the side aureole, though the abundance of low- to medium-grade metamorphic minerals (phlogopite and diopside) differs from cases 5 and 6 by \(< 5\%\).

When the aureole has a homogeneous wall-rock permeability \( (1.0 \times 10^{-6} \text{ m}^2) \) but other parameters are the same as in cases 5 and 6, the predicted \( P-T-X_{\text{CO}_2} \) histories remain again similar. However, without horizontal barriers to vertical flow, the \( \text{CO}_2 \)-rich fluid produced by devolatilization reactions migrates mainly vertically and is mostly diluted out of the inner aureole by 30 000 years. The background flow is dominated by aureole-scale circulation of fluids although strong fluid expulsion still occurs at reaction sites. Identical mineral distributions and abundances (difference < 2%) are predicted regardless of the infiltration of magmatic water into the aureole. The major difference from cases 5 and 6 is that in the homogeneous aureole, wollastonite and diopside occur in continuous zones in the side aureole, instead of being confined to aquifers.

**DISCUSSION**

The results of our models provide new insights into the metamorphic and hydrologic evolution of the Notch Peak and other aureoles. The implications of this study on a number of outstanding issues of contact metamorphism are briefly discussed.

**Geometry of aureole-scale flow**

The understanding of the geometry of fluid flow during metamorphism helps to reveal the origin of various fluids, hence the sources of ore deposits and other fluid-mobile species. Flow geometry may also reflect the thermal field, on which it is partially dependent. Fluid-flow patterns have previously been reconstructed from the distribution of mineral assemblages, shifts in stable isotope ratios, and shifts in concentration of trace elements (Cartwright & Oliver, 1994; Davis & Ferry, 1993; Ferry, 1989, 1995; Ferry et al., 2002; Ferry & Rumble, 1997; Nabelek et al., 1984; Nabelek & Labotka, 1993; Shieh & Taylor, 1969). However, the flow geometry can be deduced to only a small part of
an aureole as permitted by outcrops. The temporal evolution of the flow field is more difficult to invert from mineral and chemical data, although variable flow patterns at different stages have been suggested by recent studies (e.g. Ferry, 1996, 2000; Labotka et al., 1988).

Results of this and previous 2-D hydrodynamic studies (Cook & Bowman, 1997; Cui et al., 2001, 2002; Hanson, 1995) indicate that the fluid-flow field in contact aureoles indeed changes strongly with space and time. Shortly after emplacement of a magma body, flow will likely be radial and down-temperature away from the pluton. The outward flow is promoted by the release of magmatic water from the pluton and by thermal expansion of pore fluid in low-permeability ($<10^{-18}$ m$^2$) rocks (Hanson, 1995). The outward flow can be further enhanced by early devolatilization mineral reactions near the pluton. However, the

![Fig. 17. Snapshots of predicted thermal and $X_{\text{CO}_2}$ fields in case 6 (Table 2) at 1000 years (a), 10 000 years (b), and 30 000 years (c) (legend as in Fig. 10). Without production of magmatic water, release of metamorphic fluid can raise $X_{\text{CO}_2}$ up to 0.8 at early stages (a). But the metamorphic CO$_2$ is still mostly diluted away from the inner aureole by sedimentary fluid at later stages (b and c).](image1)

![Fig. 18. Snapshots of predicted fluid flow and pressure fields in case 6 (Table 2; legend as in Fig. 11). (a) Early heat-driven progress of mineral reactions results in local fluid expulsions at reaction fronts and outward flow in horizontal aquifers, (b) by 10 000 years background flow switches to up-temperature in the side aureole, and (c) the flow pattern remains up to 30 000 years with lower flux magnitude.](image2)
duration of the radial flow will vary with the size of the pluton and permeability structure of the aureole. In an aureole similar to the Notch Peak aureole, early stage radial flow can last about from 100 years to 10,000 years if the wall-rock permeability is about $10^{-16}$ to $10^{-17}$ m$^2$ (Cui et al., 2001, 2002), and up to 100,000 years if the permeability is $<10^{-18}$ m$^2$ (Hanson, 1995). Following the early stage down-temperature flow, the flow slowly switches to aureole-scale circulation of fluid, and mostly becomes up-temperature in the side aureole.

The thermal evolution of an aureole is more predictable at bulk permeability $<10^{-16}$ m$^2$ when heat advection by fluid is minimal, but the flow pattern can remain complex (Cui et al., 2001). Rocks far from the pluton will reach their peak temperatures long after the rocks near the pluton have done so (Figs 12a, 14a, 19a). Consequently, high-grade mineral assemblages near the pluton will primarily record the early stage, down-temperature flow, whereas the lower-grade metamorphic rocks in the outer aureole will likely record the later-stage, up-temperature flow. In an aureole with high permeability, the early down-temperature flow may have a short duration and may be overprinted by the later up-temperature flow prior to achievement of peak temperatures. Thus, metamorphic rocks in an aureole can experience several flow regimes, and the distribution of metamorphic mineral assemblages, even within a single formation, may not be caused uniquely by up-temperature or down-temperature flow. This may explain some controversies brought by the unidirectional 1-D flow models for the Notch Peak aureole (cf. Ferry & Dipple, 1992; Labotka et al., 1988; Nabelek et al., 1992; Nabelek & Labotka, 1993). Down-temperature flow should produce a sharp transition between diopside-bearing rocks and tremolite-bearing rocks, which is not always observed. Up-temperature flow should produce the coexistence of tremolite and diopside as observed in some portions of the Notch Peak aureole. Results of this study indicate mostly separation in the occurrence of tremolite and diopside but also regions of overlap of these two minerals. Thus, the predicted evolving flow system reproduces the field observations well. The evolving flow system also reproduces the oxygen isotope data (Cui et al., 2002).
Vertical fluid flow in inner aureoles has been previously documented (Ferry et al., 1998; Gerdes et al., 1995; Nabelek, 2002; Nabelek & Labotka, 1993; Roselle et al., 1999). Our predictive models indeed show that vertical flow likely dominates in a narrow zone along the side edges of a pluton (Figs 5–8, 11, & 18). The flow is mainly caused by the permeability contrast between the pluton and the wall rocks and the occurrence of a high thermal gradient there. The flow can also be enhanced by pre-existing or syn-metamorphic fracturing of the rocks (Hanson, 1995). As rocks near the pluton experience peak temperature at a very early stage, fractures associated with cooling contraction can further enhance vertical flow in the inner aureole (Hanson, 1995). The flow is nearly isothermal and can be dominated by various fluid sources as the flow regime evolves with time.

Infiltration of magmatic water into an aureole dominated by CO₂-containing sedimentary fluid complicates the flow pattern (Fig. 5). However, release of a CO₂-rich metamorphic fluid unavoidably enhances upward vertical flow around and above the pluton due to its high buoyancy (Figs 7 & 8). The fluid release also elevates fluid pressure and causes fluid expulsion at reaction fronts in all directions (Figs 11 & 18). Therefore, the release of metamorphic fluid cannot be considered as either up- or down-temperature flow. Overall, however, down-temperature fluid flow with local fluid expulsion dominates during early stage prograde metamorphism, whereas up-temperature flow becomes dominant during later stages of prograde metamorphism and throughout retrograde metamorphism. It is noted, however, that the fluid flow geometry can be influenced locally by geological structures (Ferry et al., 2002), such as folds and faults (e.g. Nabelek et al., 1992).

**Fate of metamorphic CO₂**

Calc-silicate reactions significantly contribute to the CO₂ budget in contact aureoles. For instance, wollastonite-zone rocks in the Notch Peak aureole released up to 15 wt% of rock mass as CO₂ (Labotka et al., 1988). However, the mineralogy indicates that high-grade metamorphic reactions were often driven by influx of CO₂-poor ($X_{CO2} < 0.1$) fluids in the Notch Peak (Hover-Granath et al., 1983; Labotka et al., 1988; Nabelek et al., 1992) and other aureoles, including the Alta (Cook & Bowman, 2000), Adamello (Gerdes et al., 1995), Silver Star (Ferry & Rumble,
and others (e.g. Buick et al., 2000; Ferry, 1996; Ferry et al., 1998; Heinrich & Gottschalk, 1994; Jamtveit et al., 1992). Therefore, the reaction-produced CO$_2$ must be removed from the reaction sites. Our model results show that a relatively CO$_2$-rich fluid can prevail in the inner aureole only at the early stage (< 10 000 years). Due to its greater buoyancy, CO$_2$-rich fluid strongly enhances upward flow around the pluton, hence the CO$_2$ is promptly transported away from reaction fronts and displaced by circulating water-rich sedimentary fluid. The release of magmatic water further dilutes the metamorphic CO$_2$.

Our results also show that the progress of low- to medium-grade devolatilization reactions is mainly driven by heat as a CO$_2$-rich fluid is released. The CO$_2$ released by early stage reactions next to the pluton also contributes to high CO$_2$ in the low-grade, outer-aureole rocks. Therefore, low-grade metamorphism likely occurs in the presence of a CO$_2$-rich fluid. This was observed in all the simulations, irrespective of variation in permeability structures and fluid sources. Therefore, the common petrological observation that CO$_2$-rich fluids are dominant in low-grade metamorphic zones and H$_2$O-rich fluids in high-grade metamorphic zones may be an intrinsic feature of contact aureoles. Of course, with extremely low permeability, high-grade assemblages can be produced in equilibrium with CO$_2$-rich fluids, as has occurred in the impermeable marble layers in the Notch Peak aureole (Hover-Granath et al., 1983). However, in our model the permeability of aquitards is only one order of magnitude lower than the aquifers, thus no CO$_2$-rich fluid is preserved in the model aquitards. Even a 100-fold permeability contrast cannot prevent flow of fluids through aquitards with low permeability of $1 \times 10^{-18}$ m$^2$ (Cui et al., 2001).

**Coupled fluid flow and reactions**

Local fluid-rock equilibrium is often assumed in studies of contact metamorphism. It has been suggested recently that kinetic retardation may be important during metamorphism (Bolton et al., 1999; Kerrick et al., 1991; Lasaga et al., 2000; Lasaga & Rye, 1993). Slow reaction rates of high-temperature reactions have also been indicated by field measurements (Baxter & DePaolo, 2000). Our modelling of fluid-driven reactions using a finite reaction rate gives slightly different reaction paths from those predicted assuming local equilibrium. For instance, with instaneous local equilibrium, no tremolite-forming reaction (reaction 2 in Table 3) should occur before the consumption of dolomite or quartz. However, our model predicts the growth of tremolite while talc still grows (Figs 13 & 15), and the $T$-$X_{CO_2}$ paths of rocks move quickly across the low-grade reaction curves (Fig. 12a). The overlapping reactions are likely caused by the finite reaction rate applied in our models. However, the model results predict growth of talc first and that its growth rate is higher than that of tremolite (Figs 13b & 15b). Further growth of tremolite consumes the early produced talc. Also, the model predicts that the phlogopite-out and tremolite-out reactions are followed by the diopside-in reaction, and the wollastonite-in reaction begins after the completion of diopside growth. This reaction sequence is consistent with observed assemblages in the Notch Peak and other aureoles. Application of 20 times lower or higher reaction-rate constants ($k^2$) does not change the predicted reaction progress significantly.

Prograde devolatilization reactions can be driven by heat and/or by chemically disequilibrium fluid (Dipple & Ferry, 1996; Ferry & Gerdes, 1998). Our model results show that heat mainly drives low- to medium-grade reactions, whereas fluid-driven reactions mainly occur at or after peak temperatures are reached. During early heat-driven reactions, fluid pressures at reaction fronts are elevated due to release of metamorphic fluids (Figs 12, 14 & 19), which results in fluid expulsion out of the reaction fronts and persistently high CO$_2$ concentration there. During late-stage fluid-driven reactions, fluid pressure at reaction fronts approaches the hydrostatic pressure with decrease in temperature. Hence, H$_2$O-rich magmatic or sedimentary fluid can easily infiltrate into the reaction sites, dilute the metamorphic CO$_2$, and further advance the reactions. An increase in $X_{CO_2}$ at reaction fronts is accompanied by an increase in fluid pressure, and a drop in $X_{CO_2}$ is accompanied by a drop in fluid pressure.

About 50% of wollastonite generation in rocks 200 m above the pluton is driven mainly by heat, whereas in rocks 400 m above the pluton, the wollastonite-forming reaction is driven mainly by infiltration of aqueous fluid (Figs 14 & 15). Except for the instantaneous fluid expulsion at reaction fronts, the net flow above the pluton is mainly upward, similar to the flow pattern in the Mt. Morrison pendant suggested by Ferry et al. (2001). Our model results also show that the progress of high-grade mineral reactions does not require an increase in temperature. Particularly, the wollastonite-forming reaction can occur during cooling from the peak temperature along a $T$-$X_{CO_2}$ path that is similar to the production of brucite from periclase in the Silver Star aureole (Ferry & Rumble, 1997).

The contributions of heat and fluid to the progress of medium- or high-grade mineral reactions are almost inseparable. These reactions typically progress firstly with increase in temperature and $X_{CO_2}$, and then progress with slight increase or decrease in temperature but rapid decrease in $X_{CO_2}$. Fluid-driven reactions become prevalent only when there is not enough heat to complete the reactions or when the heating rate is slower than the rate of chemical-potential change contributed by fluid flow.
Metamorphic reactions can be facilitated by increased disequilibrium fluid flux due to an increase in permeability caused by propagation of hydrofractures (e.g. Dutrow & Norton, 1995). A transient increase in porosity (up to several percent) during devolatilization reactions in calc-silicate layers can produce conduits for fluid loss or infiltration (Yardley & Lloyd, 1995). Transient enhancement of permeability by reactions may explain the common observations in many aureoles that high-grade calc-silicate layers were infiltrated by a H2O-rich fluid, but pure marble layers at the same metamorphic grade were mostly in equilibrium with a CO2-rich fluid as a closed system (e.g. Hover-Granath, 2002). The study of Cui et al. (2001) showed that transient enhancement of permeability can significantly promote fluid flow in calc-silicate layers only near the pluton. The radial expulsion of fluid that occurs at reaction fronts disrupts the flow field only locally and does not significantly distort the aureole-scale flow field (Figs 11 & 18). Overall, the analysis of the aureole-scale flow provides a useful base for understanding the highly heterogeneous flow at outcrop scales.

The Notch Peak aureole

Our simulations of the progress of coupled fluid flow and mineral reactions in the Notch Peak aureole reproduced the essential features of the observed spatial distribution of mineral assemblages, although some differences remain. For example, the predicted widths of the different metamorphic zones are systematically smaller than those observed in the Notch Peak aureole (Table 4). This may be attributed to the uncertainties in the shape and size of the pluton, the reaction rate constant, or the emplacement temperature of the magma body. A better match requires infiltration of magmatic water from the pluton into the aureole or the presence of water-rich sedimentary fluids. We favour infiltration of magmatic water because infiltration of a water-rich sedimentary fluid without magmatic water does not reproduce well the observed δ18O pattern in the aureole (Cui et al., 2002).

The models (cases 5 & 6) predict the occurrence of talc and tremolite in outer parts of the aureole. In the field, talc occurs in the fairly magnesian limestone beds of the Big Horse Member, but not in the calc-silicates of the Big Horse Member and the Weeks Formation. Minor tremolite occurs only in the upper phlogopite zone of Weeks Formation (Nabelek, 2002), but it is much more abundant in the more magnesian Big Horse Member (Hover-Granath et al., 1983). The lack of talc in the calc-silicates is attributed to the presence of Fe, which reduces the stability field of talc to XCO2 < 0.1 at the expense of the XCO2 range of the biotite-forming reaction (Nabelek, 2002). As indicated by our models, such water-rich conditions should exist only in the inner aureole if there existed a CO2-containing sedimentary fluid. Consequently, the occurrence of talc and the growth of tremolite by consumption of talc may be confined to the inner aureole where talc and tremolite are then consumed by later reactions. Furthermore, the addition of Fe also reduces the stability field of tremolite relative to diopside (Nabelek, 2002). But, our model reaction system did not account for Fe. Thus talc and tremolite are predicted to occur in the low metamorphic zones of the outer aureole (Table 4). A more than 20-fold increase in the reaction rate constant does not eliminate the occurrence of talc and tremolite in the outer aureole. However, application of a model reaction system that excludes talc-forming reaction 1 and talc-consuming reaction 2 (case 7) predicts a distribution of metamorphic mineral assemblages in the calc-silicate layers that matches better the distribution of assemblages in rocks with appreciable Fe, although tremolite is still predicted for the outer aureole (Table 4). A more refined model for the Notch Peak aureole would have to account for the presence of Fe. Incorporation of Fe into the
model reaction system would become much more difficult because of the increase variance of the model reactions.

Our model also predicts the occurrence of anorthite in the upper diopside- and wollastonite-zones, which however, is not observed in the field. The lack of observed anorthite is attributed to its consumption by the scapolite-forming reaction, which we did not account for in the models. Neither did we consider the production of vesuvianite, which occurs in the wollastonite zone (Nabelek, 2002).

CONCLUSIONS

This study investigates the transport of heat and mixed CO₂–H₂O fluid and the progress of calc-silicate reactions in contact aureoles using geological constraints from the Notch Peak aureole, Utah. Major findings include:

(1) The hydrodynamics of mixed CO₂–H₂O fluid are significantly different from those of pure-H₂O fluid. Metamorphic CO₂-rich fluid released by calc-silicate reactions in the inner aureole promotes vigorous upward flow and causes strong local fluid expulsion at reaction fronts. However, the CO₂-rich metamorphic fluid can be promptly diluted by infiltration of magmatic water and CO₂-poor sedimentary fluid.

(2) The progress of low- to middle-grade calc-silicate reactions is driven mainly by heat with rapid increases in X_CO₂ and fluid pressure, whereas the progress of the high-grade wollastonite-forming reaction is mainly driven by low X_CO₂, disequilibrium fluid at near hydrostatic fluid pressure. Down-temperature flow is likely dominant during the early stage of prograde metamorphism, whereas up-temperature fluid becomes dominant during late-stages of prograde and retrograde metamorphism.

(3) The metamorphic P–T–X_CO₂ paths of rocks are very dynamic. An early increase in X_CO₂ is accompanied by a jump of fluid pressure to a near lithostatic value due to the release of CO₂-rich fluid by heat-driven calc-silicate reactions. With the completion of low-grade reactions, X_CO₂ significantly decreases, and is accompanied by a drop in fluid pressure to a near hydrostatic value. Generally, the peak temperature experienced by rocks comes much later after the peak fluid pressure.

(4) The simulations suggest that the wollastonite-forming reaction in the Notch Peak aureole was most likely driven by the infiltration of magmatic water and has occurred even during cooling, whereas the lower-grade assemblages in the diopside and phlogopite zones were produced mainly by heat-driven reactions. Consequently, the wollastonite-zone assemblage likely formed in equilibrium with a water-rich fluid, whereas the lower-grade assemblages were formed in the presence of a high-CO₂ fluid, consistent with petrological studies (Hover-Granath et al., 1983; Nabelek, 2002; Novick & Labotka, 1990).

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