

Models for coupled fluid flow, mineral reaction, and isotopic alteration during contact metamorphism: The Notch Peak aureole, Utah

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ABSTRACT

Three different models were developed to simulate the effect of contact metamorphism and fluid-rock interaction on the prograde mineralogical and O isotopic evolution of calcareous argillites from the Notch Peak aureole, Utah. All models assume local mineral-fluid equilibrium, a steady-state temperature profile corresponding to peak metamorphic values, and the thermodynamic data for minerals and fluid of Berman (1988). The preferred model, metamorphism with flow of a time-integrated fluid flux of $2 \pm 0.5 \cdot 10^4$ mol/cm² in the direction of increasing temperature, successfully reproduces the principal petrologic and isotopic features of the aureole: (1) occurrence and positions (in map view) of diopside-in, tremolite-out, grossular-in, wollastonite-in, and quartz-out isograds; (2) stable coexistence of tremolite + calcite + quartz + diopside over an ≈ 1 km distance between the diopside-in and tremolite-out isograds; (3) variable whole-rock ¹⁸O depletions of ≈ 6 –9‰ adjacent to the contact; and (4) a gradual and irregular increase in $\delta^{18}\text{O}$ with increasing distance from the pluton. One unsuccessful model considered interaction of rock with a tiny, stagnant, fluid-filled porosity with fluid pressure equal to either lithostatic or hydrostatic pressure. Regardless of fluid pressure, the model fails to predict the position of the tremolite-out isograd; the occurrence of grossular, wollastonite, and quartz-out isograds at any position; and ¹⁸O depletions $>0.3\%$. The other unsuccessful model, flow of magmatic fluid in the direction of decreasing temperature through the aureole, fails to predict the observed range of whole-rock isotopic compositions within 0.5 km of the contact, the observed position of the diopside isograd, and the observed spatial distribution of tremolite + calcite + quartz + diopside. Results demonstrate how isotopic and petrologic data for contact aureoles can be integrated to provide quantitative constraints on the magnitude and geometry of metamorphic fluid flow.

INTRODUCTION

The emplacement of plutons at shallow levels of the crust in rocks of normal permeability almost inevitably leads to the development of hydrothermal convection systems (e.g., Norton and Knight, 1977). Consequently contact metamorphism commonly involves not only elevation of temperature in the aureole but also fluid-rock interaction. Fluid-rock interaction during contact metamorphism leaves a distinctive record in both the stable isotopic and mineralogical composition of metamorphosed rocks (cf. reviews by Rice and Ferry, 1982; Valley, 1986; Ferry, 1986, 1991). Especially good records are left in impure carbonate rocks both because their pre-metamorphic O isotopic composition is usually very different from that of normal metamorphic fluids and because interaction of siliceous carbonate rocks with aqueous fluids at elevated temperature readily drives mineral decarbonation reactions. With the recent development of models grounded in continuum mechanics that rigorously couple fluid flow to mineral and isotopic reactions in rocks (e.g., Bickle and McKenzie, 1987; Baumgartner and Rumble, 1988; Lasaga, 1989; Bickle and Baker, 1990a,

1990b; Baumgartner and Ferry, 1991; Dipple and Ferry, 1991; Ferry, 1991; Ferry and Dipple, 1991), it is now possible to interpret quantitatively the isotopic and mineralogical record of fluid-rock interaction in contact metamorphic terranes in terms of time-integrated fluid flux and flow direction relative to temperature gradients. The purpose of this report is to demonstrate how application of these models can lead to a comprehensive understanding of the mineralogical and stable isotopic structure of individual contact metamorphic terranes. The study focuses specifically on calcareous argillites of the Big Horse Limestone Member of the Orr Formation in the Notch Peak contact aureole, Utah. The Notch Peak aureole was chosen because there is exceptionally thorough published documentation of its geology, mineralogy, and whole-rock and stable isotope geochemistry.

GEOLOGY, PETROLOGY, AND O ISOTOPE GEOCHEMISTRY OF THE NOTCH PEAK CONTACT AUREOLE

The composite Notch Peak stock consists of granite and quartz monzonite (Nabelek et al., 1986) and intruded

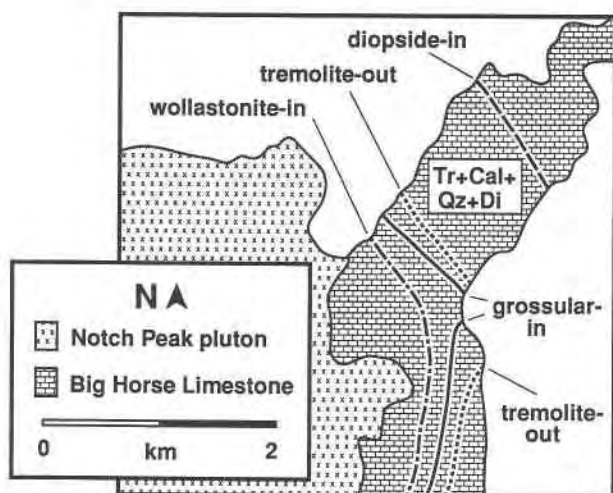


Fig. 1. Simplified geologic and metamorphic map of the eastern and northeastern portion of the Notch Peak contact metamorphic aureole, Utah (modified after Fig. 5 of Hover-Granath et al., 1983). Models described in text attempt to reproduce the observed sequence of four isograds, the spacing between isograds and the pluton-metasediment contact, and the occurrence of tremolite (Tr) + calcite (Cal) + quartz (Qz) + diopside (Di) in rocks between the diopside-in and tremolite-out isograds over a distance of ≈ 1 km.

the Cambrian Big Horse Limestone Member of the Orr Formation in Jurassic time (Hover-Granath et al., 1983). The Big Horse Limestone Member is composed of gently dipping interbedded siliceous limestones and calcareous argillites and their contact-metamorphosed equivalents.

The mineralogical and petrologic effects of contact metamorphism are described by Hover-Granath et al. (1983) and Labotka et al. (1988a). The first-order petrologic features of metamorphosed calcareous argillites in the contact aureole are summarized in Figure 1 and Table 1: (1) the appearance, with increasing proximity to the

pluton-metasediment contact, of diopside at the diopside isograd; (2) coexistence of reactants and products of the diopside-forming reaction (tremolite + calcite + quartz + diopside) over a distance of ≈ 1 km in the diopside zone; (3) the disappearance of tremolite at the tremolite-out isograd; (4) the appearance of grossular or vesuvianite or both at the grossular + vesuvianite isograd; (5) the appearance of wollastonite at the wollastonite isograd; and (6) the absence of reactants of the wollastonite-forming reaction (quartz is consumed) in the innermost part of the aureole. The distances of the isograds from the pluton-metasediment contact (Table 1) were measured in the eastern part of the contact aureole from Figure 5 of Hover-Granath et al. (1983), which is reproduced in simplified form as Figure 1 of this report. Isograds in the southern portion of the aureole are bunched and difficult to interpret. Inferred pressure of contact metamorphism was 2 kbar, and the maximum temperature at the pluton-metasediment contact was ≈ 600 °C (Labotka et al., 1988a).

The stable isotopic effects of contact metamorphism on the Big Horse Limestone Member were reported by Nabelek et al. (1984). The first-order isotopic features of argillites in the contact aureole are summarized in Table 1 and Figure 2: (1) whole-rock $\delta^{18}\text{O}$ decreases continuously from $\approx 19\text{‰}$ (SMOW) in unmetamorphosed samples 2–5 km from the pluton to 8–15‰ within ≈ 400 m of the contact and (2) the $\delta^{18}\text{O}$ of argillites close to the pluton is not uniform but varies over a significant range of $\approx 7\text{‰}$. In contrast to the argillites, the O isotope composition of interbedded limestones is uniform throughout the aureole and was unaffected by contact metamorphism (Nabelek et al., 1984). The difference in isotopic composition between argillites and limestones led Nabelek et al. (1984) to conclude that fluid flow was highly channelized during metamorphism, with enhanced flow along argillite layers and little or no flow along the limestone layers.

The whole-rock major- and minor-element geochem-

TABLE 1. First-order isotopic and petrologic features of the Notch Peak contact aureole

Feature	Observation*	No flow models**		Up-temperature flow model $q_m = (1-3) \cdot 10^4$ mol/cm ²	Down-temperature flow models†	
		$P_t = P_l$	$P_t = P_h$		$q_m = 2 \cdot 10^3$ mol/cm ²	Model of Labotka et al. (1988a)
Appearance of diopside	$\approx 1.4-2.2$ km	1.80 km	1.80 km	1.80 km	0.49 km	0.59 km
Tremolite + calcite + quartz + diopside stable	$\approx 1-2$ km	0.21–1.80 km	0.46–1.80 km	0.98–1.80 km	0.49 km	0.59 km
Disappearance of tremolite	$\approx 0.7-1.2$ km	0.21 km	0.46 km	0.98–1.18 km	0.49 km	0.59 km
Appearance of grossular or vesuvianite	$\approx 0.6-1.1$ km	not predicted	not predicted	0.86–1.16 km	0.20 km	0.43 km
Appearance of wollastonite	$\approx 0.4-0.8$ km	not predicted	not predicted	0.47–0.66 km	0.19 km	0.42 km
Wollastonite-forming reaction complete	$< \approx 0.4-0.8$ km	not predicted	not predicted	0.34–0.52 km	0.19 km	0.42 km
$\delta^{18}\text{O}_{\text{rock}}$ at or near contact	$\approx 8-15\text{‰}$	18.7‰	18.7‰	9.0–15.4‰	9.3‰	9.3‰
$\delta^{18}\text{O}_{\text{rock}} \approx 1$ km from contact	$\approx 12-19\text{‰}$	19.0‰	19.0‰	11.8–15.4‰	19.7‰	19.3‰

* Isograds from east and northeast side of contact aureole (Hover-Granath et al., 1983; Fig. 1); isotopic compositions from Nabelek et al. (1984). Distances measured away from the pluton with 0 at the pluton-metasediment contact.

** Results for fluid pressure (P_f) equal lithostatic pressure (P_l) and fluid pressure equal hydrostatic pressure (P_h).

† Results in first column for time-integrated H_2O flux of $2 \cdot 10^3$ mol/cm² outward from the contact ($z = 0$); model of Labotka et al. (1988a) refers to perfect chemical equilibration of argillite with magmatic H_2O in the innermost 400 m of the contact aureole and a time-integrated flux of 900 mol/cm² H_2O outward from a position at $z = 400$ m.

istry of the contact metamorphosed Big Horse Limestone Member was investigated by Labotka et al. (1988b). Except within a few meters of the pluton, contact metamorphism of all carbonate rocks was isochemical or nearly so.

INTEGRATED MINERALOGICAL AND ISOTOPIC MODELS OF CONTACT METAMORPHISM

Summary of approach

Fluid-rock interaction during metamorphism in the Notch Peak aureole was investigated by considering a model rock with bulk chemical composition that is a slightly simplified analogue to that of average argillite. The metamorphism is simulated in a one-dimensional contact aureole where the distribution of temperature with distance throughout the duration of fluid flow and metamorphism is similar to the distribution of peak temperatures in the Notch Peak aureole. Fluid is considered a binary $\text{CO}_2\text{-H}_2\text{O}$ solution. Equations grounded in transport theory are used to predict mineralogical and isotopic alteration that result from various types of fluid-rock interaction (e.g., no fluid flow; flow in the direction of increasing temperature; flow in the direction of decreasing temperature). Predicted mineralogical and isotopic alteration are then compared with observed petrologic and isotopic features of the Notch Peak aureole (Figs. 1, 2; Table 1) to determine which type of fluid-rock interaction best accounts for the observed features. The goal of the study was to identify the simplest possible model that reproduces the first-order petrologic and isotopic features of the aureole.

Input parameters to simulations

Composition and mineralogy of model rock. The bulk composition of an analogue argillite in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2\text{-H}_2\text{O}$ was calculated from the average mode of samples from the wollastonite zone (Table 4 of Labotka et al., 1988a) and simplified compositions of the constituent minerals (their Table 3). A relatively small amount of K_2O (1.3 oxide mol% on an $\text{H}_2\text{O-CO}_2$ -free basis) was simply omitted for two reasons. First, the K-free analogue composition is capable of reproducing the first-order petrologic features of the contact aureole (i.e., diopside, tremolite-out, grossular, and wollastonite isograds). Second, regardless of the type of fluid-rock interaction, all models of metamorphism involving a K-bearing analogue composition fail to reproduce the observed subassemblage phlogopite + calcite + quartz + tremolite + potassium feldspar + diopside in the diopside zone. The subassemblage never develops because current thermodynamic data bases (e.g., Berman, 1988) predict that it is unstable at all temperatures at 2 kbar in the system $\text{CaO-K}_2\text{O-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2\text{-H}_2\text{O}$ (CKMASCH), a prediction unequivocally confirmed by the experimental results of Wones (1970). The assemblage biotite + calcite + quartz + calcium amphibole + potassium feldspar + calcium pyroxene is stabilized in metamorphic rocks by non-CKMASCH components (e.g.,

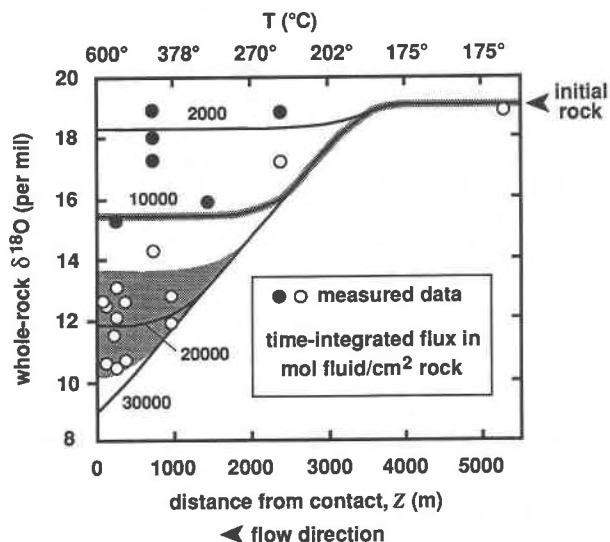


Fig. 2. Measured and calculated whole-rock O isotope compositions of calcareous argillites as a function of distance from the pluton-metasediment contact ($Z = 0$). Measured distance- $\delta^{18}\text{O}$ data from Nabelek et al. (1984), Table 1, and Labotka et al. (1988a), Table 1. Curves calculated from Equation 1 in text for four different values of time-integrated mole fluid flux and flow in the direction of increasing temperature (curve for $q_m = 10000$ mol/cm 2 highlighted by shading). Curves for the four different fluxes superimpose along their inclined portions and at distances >4000 m. Most observed ^{18}O depletions within 500 m of the pluton in the Notch Peak aureole can be explained by flow of $(1.5\text{--}2.5) \cdot 10^4$ mol/cm 2 fluid through the contact aureole and up-temperature flow (shaded area). Only six of 20 analyzed samples (black circles) deviate by more than $\approx 1\%$ from values predicted by this preferred model. Temperatures calculated from equation for temperature profile in Table 2.

Hewitt, 1973). The inclusion of K in an analogue rock composition therefore appeared to introduce unnecessary complications.

The mineral content of the analogue protolith was considered tremolite + anorthite + calcite + quartz; relative amounts of the minerals (Table 2) were computed from the bulk composition of the analogue argillite and the mineral formulas in Table 3 of Labotka et al. (1988a). This low-grade metamorphic assemblage was chosen because it is the simplest assemblage that reproduces the four mapped isograds (Fig. 1) with the fewest number of prograde reactions, and it is consistent with the nascent diopside zone assemblage of Labotka et al. (1988a, their Table 5). Models of metamorphism considered the development of diopside, grossular, and wollastonite from the protolith mineral assemblage. Vesuvianite was neglected because there exists no data for its thermodynamic properties consistent with those of Berman (1988).

Mineral reactions and mineral-fluid equilibria. Figure 3 illustrates all possible stable reactions involving tremolite, calcite, anorthite, quartz, diopside, grossular, wollastonite, and $\text{CO}_2\text{-H}_2\text{O}$ fluid at 0.75 and 2 kbar and $T = 350\text{--}650$ °C. The reactions constitute isograd reactions in

TABLE 2. Parameterization of integrated isotopic and mineralogical models of contact metamorphism

Parameter	Source
Temperature profile: T (K) = $873 - 0.3336Z$ (m) + $1.530 \cdot 10^{-4}Z^2 - 4.909 \cdot 10^{-8}Z^3 + 8.426 \cdot 10^{-12}Z^4 - 5.391 \cdot 10^{-16}Z^5$ (0–4 km)	1
Ambient temperature: 448 K ($Z \geq 4$ km)	2
Initial whole-rock $\delta^{18}\text{O}$: +19‰	3
$\delta^{18}\text{O}_{\text{rock}} - \delta^{18}\text{O}_{\text{H}_2\text{O}} = 2.78 \cdot 10^6/T^2 - 2.89$	4
$\delta^{18}\text{O}_{\text{rock}} - \delta^{18}\text{O}_{\text{CO}_2} = 1.8034 \cdot 10^6/T^2 - 10.611 \cdot 10^3/T + 2.7798$	4
Calcite + quartz = wollastonite + CO_2 equilibrium: $X_{\text{CO}_2} = 3.0808 \cdot 10^{-56} T^{18.6197}$ ($T = 698\text{--}873$ K)	5
Anorthite + quartz + 2calcite = grossular + 2 CO_2 equilibrium: $X_{\text{CO}_2} = 1.4318 \cdot 10^{-46} T^{15.3221}$ ($T = 623\text{--}853$ K)	5
Tremolite + 3calcite + 2quartz = 5diopside + 3 CO_2 + H_2O equilibrium: $X_{\text{CO}_2} = 9.3705 \cdot 10^{-71} T^{23.9788}$ ($T = 623\text{--}768$ K)	5
$X_{\text{CO}_2} = 1.4776 \cdot 10^{-87} T^{29.8023}$ ($T = 768\text{--}808$ K)	
Anorthite + wollastonite + calcite = grossular + CO_2 equilibrium: $X_{\text{CO}_2} = 1.7360 \cdot 10^{-22} T^{7.1053}$ ($T = 843\text{--}873$ K)	5
Initial rock (mol/kg): 0.5146 anorthite + 0.1962 tremolite + 3.3088 quartz + 4.9818 calcite	6

Note: 1 = Similar to curve in Labotka et al. (1988a), their Figure 6, extrapolated smoothly to ≈ 175 °C at 4000 m. 2 = Average of 200 °C and value listed in Labotka et al. (1988a), their Table 6. 3 = Nabelek et al. (1984), greatest value reported for "unmetamorphosed" samples. 4 = Friedman and O'Neil (1977) for calcite. 5 = Calculated for $P = p_{\text{CO}_2} + p_{\text{H}_2\text{O}} = 2000$ bars from data in Berman (1988) with $\text{CO}_2\text{-H}_2\text{O}$ mixing after Kerrick and Jacobs (1981). 6 = Calculated on a K-free basis using average wollastonite zone mineral abundances in Table 4 and idealized mineral compositions in Table 3 of Labotka et al. (1988a).

the analogue argillite. Simple analytical expressions for T - X_{CO_2} conditions of four reactions are listed in Table 2 (X_{CO_2} is the mole fraction CO_2 in fluid). Except for the high-temperature expression for the diopside-forming reaction, expressions reproduce X_{CO_2} values calculated from the data of Berman (1988) over the stated range of temperature to within ± 0.005 . For a given X_{CO_2} the high-temperature expression for the diopside-forming reaction reproduces equilibrium conditions calculated from Berman's (1988) data to ± 1 °C or better in the stated temperature range. The 623-K limit on two equations represents the low-temperature limit of the applicability of Berman's data base and Kerrick and Jacobs' (1981) equation of state for $\text{CO}_2\text{-H}_2\text{O}$ fluids to calculation of mixed volatile mineral-fluid equilibria.

Isotopic composition of model rock and fluid-rock isotope exchange equilibria. The initial O isotope composition of the analogue argillite ($\delta^{18}\text{O} = 19\text{‰}$) was taken as the maximum value of all "unmetamorphosed" argillites reported by Nabelek et al. (1984). Fluid-rock O isotope exchange reaction was approximated by the system calcite- H_2O - CO_2 because the fractionation of ^{18}O between calcite and H_2O - CO_2 fluid is intermediate between that of quartz on one hand and diopside, anorthite, and amphibole on the other (Friedman and O'Neil, 1977; Chiba et al., 1989). From a more fundamental standpoint, calcite was chosen as a model for argillite in computations of isotopic alteration because there is no analytical model that rigorously couples fluid flow along temperature gradients with simultaneous mineral decarbonation reactions and mineral-fluid isotopic exchange. The isotopic effects of prograde reactions in argillite, however, are small ($\leq 2\text{‰}$, Nabelek et al., 1984). Because the goal of models developed in this study is to explain ^{18}O depletions of up to 6–8‰ in argillite, the neglect of decarbonation reactions in computation of isotopic alteration is considered acceptable. The temperature dependencies of O isotope fractionation between calcite and H_2O and between calcite and CO_2 (Table 2) were taken from Friedman and O'Neil (1977).

Flow path and temperature profile. Isotopic data unambiguously demonstrate that metamorphic fluid flow in the Notch Peak aureole was largely confined to the calcareous argillites (Nabelek et al., 1984). Bedding is subhorizontal in the contact aureole (Hover-Granath et al., 1983). Numerical models of pluton-driven hydrothermal circulation indicate that fluid flow in the country rock should be radial to the pluton (e.g., Norton and Knight, 1977). The one-dimensional models of contact metamorphic fluid flow in this study therefore consider that flow was subhorizontal and radial to the pluton. The specific goals of the models are to (1) reproduce the sequence and spacing of isograds and mineral assemblages along a ground-surface transect perpendicular to isograds in Figure 1 and (2) to reproduce the profile of whole-rock O isotope compositions plotted as a function of radial distance from the pluton-metasediment contact (Fig. 2). Distance along the one-dimensional flow path is represented by Z measured from 0 at the pluton-metasediment contact.

Variation in temperature along the flow path must be specified in the models. For a geothermal gradient of 25 °C/km, the ambient temperature at a depth that corresponds to a pressure of 2 kbar would be ≈ 200 °C. Labotka et al. (1988a), however, suggest that the ambient temperature prior to metamorphism was 150 °C (their Table 6). As a compromise, a value of 175 °C was adopted. Prograde contact metamorphism therefore involved peak temperatures in the range 175–600 °C. The equation for the temperature profile during metamorphism in Table 2 is a smooth curve between $T = 600$ °C at $Z = 0$ (the contact) and 175 °C at $Z = 4$ km ($T = 175$ °C for $Z > 4$ km). The curve is similar both to the locus of radial distance-peak temperature points from a thermal model of the aureole and to the ground-surface locus of temperature-radial distance points recorded by calcite-dolomite geothermometry (Labotka et al., 1988a, their Fig. 6). Because fluid flow during metamorphism was subhorizontal parallel to lithologic layering and radial to the pluton, the ground-surface temperature profile represented by the

equation in Table 2 was taken as the temperature profile along the metamorphic fluid flow path. The justification for and consequences of basing calculations on a steady-state temperature profile are discussed in a later section.

Metamorphism with no fluid flow

For completeness the first models considered correspond to progressive metamorphism without fluid flow. One model considers fluid pressure (P_f) equal to lithostatic pressure (P_l); the other considers P_f equal to hydrostatic pressure (P_h).

$P_f = P_l = 2$ kbar. The conventional model of metamorphism involves increasing temperature at $P_f = P_l$ in the absence of infiltration of rock by fluids. If the analogue argillite, initially containing a tiny porosity filled with H₂O-rich CO₂-H₂O fluid (left, for example, from sedimentation and diagenesis), is heated to peak temperatures and local mineral-fluid equilibrium is attained, the rock's mineralogical evolution can be predicted from Figure 2 and equations in Table 2. The temperature at which reaction begins is constrained by the observed position of the diopside isograd in the field ($Z = 1.8 \pm 0.4$ km) and the model temperature profile: $T = 287 (\pm 41)^\circ\text{C}$. The assemblage tremolite + anorthite + calcite is stable at $T < 287^\circ\text{C}$ ($Z > 1.8$ km), and the assemblage tremolite + anorthite + quartz + calcite + diopside is stable between 287°C and the maximum temperature on the curve for the diopside-forming reaction, 537°C ($Z = 0.21$ km). If porosity is very small, the progress of the diopside-forming reaction in the interval $T = 287\text{--}537^\circ\text{C}$ is correspondingly small. Virtually all tremolite reacts with calcite and quartz to form diopside at 537°C . At $T > 537^\circ\text{C}$ argillite is composed of diopside + calcite + quartz + anorthite and no further reactions occur below 600°C ($Z < 0.21$ km). Specifically, neither grossular nor wollastonite develop. The final relationship between temperature and X_{CO_2} of the pore fluid at the peak of metamorphism is illustrated by the thick shaded curve in Figure 3a for $T = 350\text{--}600^\circ\text{C}$.

If porosity is very small, the O isotope composition of argillite remains $+19\text{‰}$ at $T < 537^\circ\text{C}$ ($Z > 0.21$ km). There is a small shift in isotopic composition (-0.3‰ $\delta^{18}\text{O}$) caused by the diopside-forming reaction at 537°C , computed from the expression for Rayleigh distillation (Eq. 5 of Rumble, 1982), the composition of fluid at 537°C ($X_{\text{CO}_2} = 0.75$, Fig. 3a), and expressions for O isotope fractionation in Table 2. At $T = 537\text{--}600^\circ\text{C}$ ($Z = 0\text{--}0.21$ km) model argillite has $\delta^{18}\text{O} = +18.7\text{‰}$.

$P_f = P_h = 0.75$ kbar. Alternatively, progressive contact metamorphism could occur with increasing temperature in the absence of infiltration but with $P_f = P_h$ ($= 0.75$ kbar for a depth in crustal rocks of normal density corresponding to $P_l = 2$ kbar). Such a circumstance could develop, for example, if rocks were in chemical communication with vertical fluid-filled fractures that extended to the Earth's surface. An approximate thermodynamic treatment of mineral-fluid equilibria when $P_f \neq P_l$ is to consider that P_f is the determining pressure (Bruton

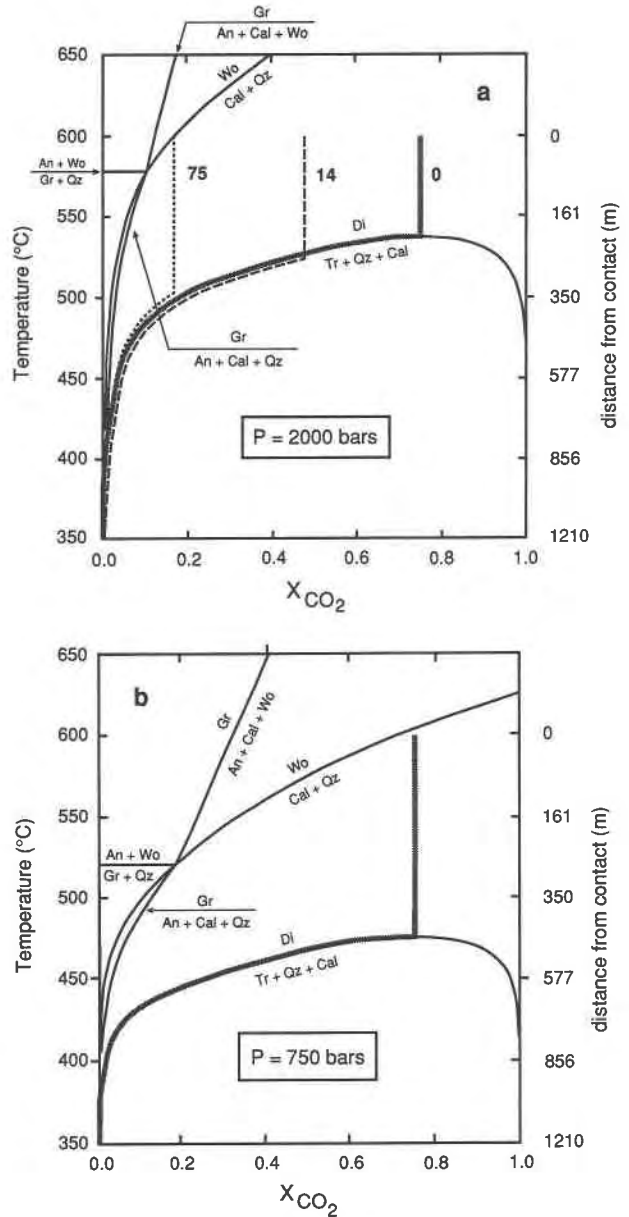


Fig. 3. Isobaric T - X_{CO_2} diagrams illustrating phase equilibria among tremolite (Tr), calcite (Cal), quartz (Qz), diopside (Di), grossular (Gr), wollastonite (Wo), and H₂O-CO₂ fluid at 350–650 °C calculated from data in Berman (1988) and the equation of state for H₂O-CO₂ fluid of Kerrick and Jacobs (1981): (a) 2000 bars pressure; (b) 750 bars pressure. Thick shaded curves in a and b delineate the T - X_{CO_2} path of fluid for the case of model prograde metamorphism in the absence of fluid flow ($q_m = 0$). Dashed and dotted paths in a delineate the T - X_{CO_2} conditions of the system after passage of 14 and 75 mol fluid/cm² rock, respectively, flowing in the direction of increasing temperature (see text for details). Distance from contact computed from equation for temperature profile in Table 2.

and Helgeson, 1983). The mineralogical evolution of argillite under these conditions therefore can be predicted from the reaction curves for 0.75 kbar in Figure 3b, and the evolution is similar to that under conditions $P_f = P_i$. Tremolite, however, is consumed at a lower temperature, 475 °C ($Z = 0.46$ km). At $T > 475$ °C model argillite is composed of diopside + calcite + quartz + anorthite and no further reactions occur below 600 °C ($Z < 0.46$ km). Neither grossular nor wollastonite develop. The final relationship between temperature and X_{CO_2} of the pore fluid at the peak of metamorphism is illustrated by the thick shaded curve in Figure 3b for $T = 350$ –600 °C.

There is a small shift in O isotopic composition, -0.3% $\delta^{18}\text{O}$, caused by the diopside-forming reaction, computed by the same procedure used in the model for metamorphism at $P_f = P_i$. At $T = 475$ –600 °C ($Z = 0$ –0.46 km) model argillite has $\delta^{18}\text{O} = +18.7\%$.

Metamorphism with fluid flow in the direction of increasing temperature

A second set of models considers flow of fluid inward toward the Notch Peak pluton during contact metamorphism in the direction of increasing temperature. Both the degree of O isotopic alteration and the identity and progress of prograde devolatilization reactions in the contact aureole were computed for a range of time-integrated fluid fluxes.

Coupled fluid flow and isotopic reaction. A number of studies have rigorously coupled fluid flow and chemical reaction in porous media, and they fundamentally follow the same analytical approach (Lichtner, 1985; Bickle and McKenzie, 1987; Baumgartner and Rumble, 1988; Lasey and Blattner, 1988; Norton, 1988; Bickle and Baker, 1990a, 1990b). Solution of the equations is greatly simplified by making several assumptions appropriate for the elevated temperatures and relatively large spatial scales of fluid-rock interaction during metamorphism: (1) local mineral-fluid equilibrium; (2) negligible mass transfer by diffusion and dispersion; and (3) one-dimensional flow. To further simplify analysis, a steady-state temperature profile along the flow path was assumed. Discussion and justification of these simplifications appear in a later section.

Under these circumstances, the relationship between the whole-rock O isotope alteration at any point, z , in the flow system and the time-integrated mole fluid flux is

$$\delta^{18}\text{O}_{i,\text{rk}}(z) - \delta^{18}\text{O}_{f,\text{rk}}(z) = \delta^{18}\text{O}_{i,\text{fl}}(z - B) - \delta^{18}\text{O}_{i,\text{fl}}(z) \quad (1)$$

where the first subscript to δ refers to initial (i) conditions prior to fluid flow or final (f) conditions after flow is complete; the second subscript refers to rock (rk) or fluid (fl); $B = (q_m N_f / V_r)$; q_m is the mole fluid flux (mol fluid/cm² rock), integrated over the entire duration of flow; N_f is the number of moles O per mole fluid; and V_r is the number of moles O per unit volume of rock (see Bickle and Baker, 1990a, 1990b, or Dipple and Ferry, 1991, for further detail). Equation 1 neglects shifts in isotope composition caused by devolatilization reactions. As argued

earlier, this simplification is an acceptable first approximation for contact metamorphism in the Notch Peak aureole.

Metamorphic fluids during contact metamorphism in the Notch Peak aureole were nearly pure H₂O (Labotka et al., 1988a). Prior to fluid flow, model argillite is considered to contain initially a small porosity filled with H₂O fluid in isotopic exchange equilibrium with calcite rock of $\delta^{18}\text{O} = +19\%$. For H₂O fluid and calcite rock, $N_f = 1$ mol O/mol fluid and $V_r = 0.081$ mol O/cm³ rock (Berman, 1988). For fluid flow in the direction of increasing temperature, the spatial coordinate z in Equation 1 is antiparallel to distance variable Z measured from the pluton-metasediment contact. After fluid flow commences, the O isotopic alteration of rock as a function of z (or Z) and T can be computed from Equation 1 for specified values of time-integrated mole flux, q_m . Results are illustrated in Figure 2. Little O isotopic alteration occurs if $q_m < \approx 2 \cdot 10^3$ mol/cm² ($< 1\%$ $\delta^{18}\text{O}$). For $q_m = (1.5$ – $2.5) \cdot 10^4$ mol/cm², fluid flow results in ¹⁸O depletions near the pluton-metasediment contact of 6–9‰ $\delta^{18}\text{O}$, spanning the range of most observed values. Fourteen of the 20 measurements in Figure 2 are within $\approx 1\%$ of values predicted by the model for flow of $(1.5$ – $2.5) \cdot 10^4$ mol/cm² fluid through the contact aureole in the direction of increasing temperature (open circles). The six discordant data points (filled circles, Fig. 2) can be explained if time-integrated fluid fluxes were spatially variable during metamorphism in the outer portion of the aureole. Specifically, taken at face value, the filled circles in Figure 2 imply that time-integrated fluid fluxes were as low as $(0.2$ – $1) \cdot 10^4$ mol/cm² in some parts of the contact aureole more than 500 m from the contact.

The maximum predicted reduction in $\delta^{18}\text{O}$, -10% , occurs when $q_m = 3.25 \cdot 10^4$ mol/cm². For $q_m = 3.25 \cdot 10^4$ mol/cm², the model contact aureole is fully equilibrated isotopically with the input fluid (H₂O fluid in isotopic exchange equilibrium with initial unaltered calcite at 175 °C), and no further reduction in whole-rock $\delta^{18}\text{O}$ occurs even if $q_m > 3.25 \cdot 10^4$ mol/cm².

Coupled fluid flow and mineralogical reaction. The mineral content of the system prior to flow is considered to be that produced by heating model argillite, with a small fluid-filled porosity, to peak metamorphic temperatures in the absence of fluid flow. The pore fluid could be left, for example, from sedimentation and diagenesis. The initial pore fluid composition is specified so that diopside develops at the position observed in the field ($Z = 1.8$ km), given the model temperature profile in Table 2 ($T = 287$ °C at $Z = 1.8$ km) and the T - X_{CO_2} conditions of the tremolite + calcite + quartz + diopside + fluid equilibrium. Using the relevant equation for mineral-fluid equilibrium from Table 2, calculated fluid composition is $X_{\text{CO}_2} = 7 \cdot 10^{-5}$. Although the value is uncertain because calculations applied the T - X_{CO_2} expression outside its temperature limits, the exact value is unimportant in subsequent calculations provided that the T - X_{CO_2} curve for the anorthite + calcite + quartz + grossular equilibrium

continues to asymptotically approach $X_{\text{CO}_2} = 0$ at $T < 350$ °C. After heating, pore fluid composition is represented as a function of distance and temperature by the thick shaded curve in Figure 3a. Fluid flow in the direction of increasing temperature toward the pluton therefore involves infiltration of H_2O -rich fluid distal from the pluton into the contact aureole. Mineral-fluid reaction results from continuous adjustment of fluid composition to increasing values of X_{CO_2} specified both by equilibrium between reactants and products and the increasing temperature along the flow path (cf. Fig. 3a). Under these circumstances, assuming local mineral-fluid equilibrium at each point at all times, negligible mass transfer by diffusion and dispersion, and one-dimensional flow, the relationship between progress, ξ , of a decarbonation-dehydration reaction at any point in the flow system and q_m is

$$q_m = \frac{\xi[\nu_{\text{CO}_2} - X_{\text{CO}_2}(\nu_{\text{CO}_2} + \nu_{\text{H}_2\text{O}})]}{(\partial X_{\text{CO}_2}/\partial T)_P(dT/dz) + (\partial X_{\text{CO}_2}/\partial P)_T(dP/dz)} \quad (2)$$

where ν_{CO_2} and $\nu_{\text{H}_2\text{O}}$ are stoichiometric coefficients of CO_2 and H_2O in the reaction, z is the spatial coordinate oriented parallel to the direction of flow, and ξ is measured with reference to 1 cm^3 rock (see Baumgartner and Ferry, 1991, or Ferry and Dipple, 1991, for further detail). For fluid flow in the direction of increasing temperature, the spatial coordinate z in Equation 2 is antiparallel to distance variable Z measured from the pluton-metasediment contact. In order for fluid to have flowed in the contact aureole there must have been a decrease in fluid pressure (hydraulic head) along the flow path during metamorphism. Because metamorphic fluid flow was nearly horizontal and because normally $(\partial X_{\text{CO}_2}/\partial P)_T \ll (\partial X_{\text{CO}_2}/\partial T)_P$, for geologically relevant decarbonation-dehydration reactions (e.g., Ferry and Dipple, 1991), the term $(\partial X_{\text{CO}_2}/\partial P)_T(dP/dz)$ in Equation 2 was ignored.

Mineralogical effects of fluid flow as a function of time-integrated flux were computed for model argillite using Equation 2 and equations in Table 2 over the temperature range 350–600 °C. For all values of q_m considered, argillite is composed of tremolite + calcite + anorthite + quartz + diopside at 350 °C and a range of $T > 350$ °C (cf. Fig. 3a). For model rock with protolith mineral content listed in Table 2, tremolite is exhausted by the diopside-forming reaction when $\xi_{\text{di}} = 5.39 \cdot 10^{-4} \text{ mol/cm}^3$. The model tremolite-out isograd therefore always occurs at the position where $(q_m)(\partial X_{\text{CO}_2}/\partial T)_P(dT/dz)/(3 - 4X_{\text{CO}_2}) = \xi_{\text{di}} = 5.39 \cdot 10^{-4} \text{ mol/cm}^3$. If $q_m = 14 \text{ mol/cm}^2$, for example, the tremolite-out isograd is located at $Z = 0.25 \text{ km}$ ($T = 525$ °C; $X_{\text{CO}_2} = 0.46$; cf. dashed curve, Fig. 3a). As a corollary, taking the position of the diopside isograd from field observation, the assemblage tremolite + calcite + anorthite + quartz + diopside would be stable in the interval $Z = 0.25$ – 1.80 km when $q_m = 14 \text{ mol/cm}^2$.

With increasing time-integrated flux, the tremolite-out isograd migrates away from the pluton and the X_{CO_2} of fluid along the flow path evolves to more H_2O -rich compositions. When $q_m = 75 \text{ mol/cm}^2$, for example, the trem-

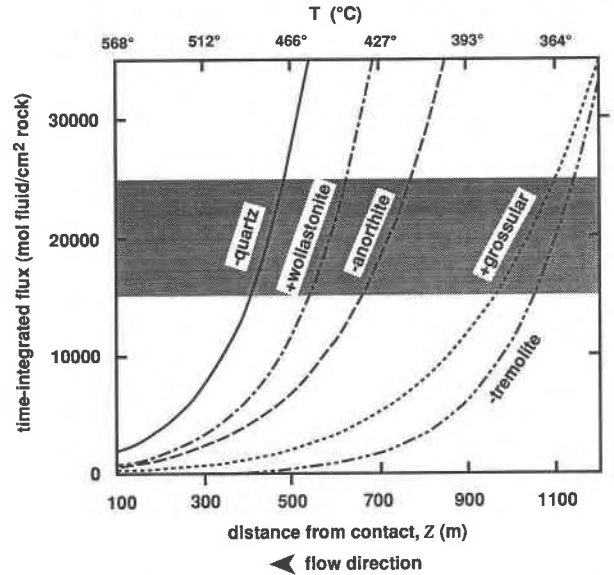


Fig. 4. Positions of isograds calculated from Equation 2 as a function of time-integrated fluid flux flowing in the direction of increasing temperature (see text for details). The + sign indicates appearance of mineral with increasing grade of metamorphism (decreasing Z); the - sign indicates disappearance of mineral. Observed positions of the isograds in the Notch Peak aureole can be explained by up-temperature flow of $(1.5$ – $2.5) \cdot 10^4 \text{ mol/cm}^2$ fluid through the contact aureole (shaded area). Temperatures calculated from equation for temperature profile in Table 2.

olite-out isograd occurs at 0.35 km ($T = 500$ °C; $X_{\text{CO}_2} = 0.18$) and wollastonite first appears at the contact (cf. dotted curve, Fig. 3a). For model rock with protolith mineral content listed in Table 2, the wollastonite-forming reaction progresses at the point $Z = 0$ until $(q_w)(\partial X_{\text{CO}_2}/\partial T)_P(dT/dz)/(1 - X_{\text{CO}_2}) = \xi_{\text{wo}} = 8.01 \cdot 10^{-3} \text{ mol/cm}^3$, where q_w is the time-integrated flux through the metamorphic system after wollastonite first forms. Accordingly, reaction is first complete at the contact (quartz is exhausted) when $q_w = 527 \text{ mol/cm}^2$. A model quartz-out isograd therefore first appears at the contact after a time-integrated flux $q_m = 75 + 527 = 602 \text{ mol/cm}^2$ has flowed through the system.

Progress of each of the prograde mineral reactions in Table 2, and the corresponding positions of isograds in the model system were evaluated as a function of increasing time-integrated flux in a similar way. Results are presented for $Z > 100 \text{ m}$ in Figure 4. Results for $Z < 100 \text{ m}$ are more complicated, are irrelevant to the discussion, and were omitted for clarity. Because of the temperature limitations of equations in Table 2, computations were terminated when the tremolite-out isograd reached a position corresponding to 350 °C ($Z = 1.21 \text{ km}$). For a value of $q_m = 1.5 \cdot 10^4 \text{ mol/cm}^2$, the quartz-out isograd occurs at 0.40 km , the minimum distance consistent with observation (Table 1), whereas for $q_m = 2.5 \cdot 10^4 \text{ mol/cm}^2$, the tremolite-out isograd occurs at 1.2 km , the maximum

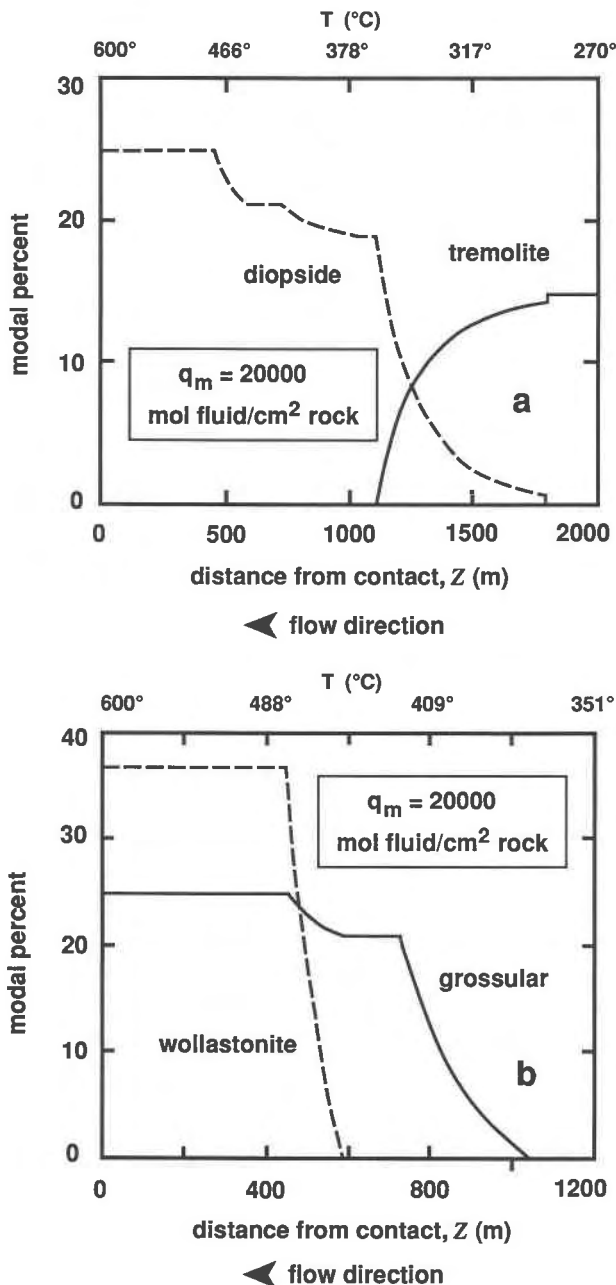


Fig. 5. Modes for diopside and tremolite (a) and grossular and wollastonite (b) as a function of distance from the pluton-metasediment contact calculated from Equation 2 in text for the case of flow of $2 \cdot 10^4$ mol/cm² fluid in the direction of increasing temperature through the contact aureole. The increase in diopside at distances <1.1 km and the increase in grossular at distances <0.6 km results from decrease in volume of the rock rather than from participation of the two minerals in reactions. Calculated distribution of minerals agrees with observed distribution in the contact aureole. Temperatures computed from equation for temperature profile in Table 2.

distance consistent with observation. Up-temperature fluid flow results in positions of isograds spanning the range of observed values (Table 1) when $q_m = (1.5-2.5) \cdot 10^4$ mol/cm² (shaded region of Fig. 4), consistent with the analysis of O isotopic alteration (shaded area of Fig. 2).

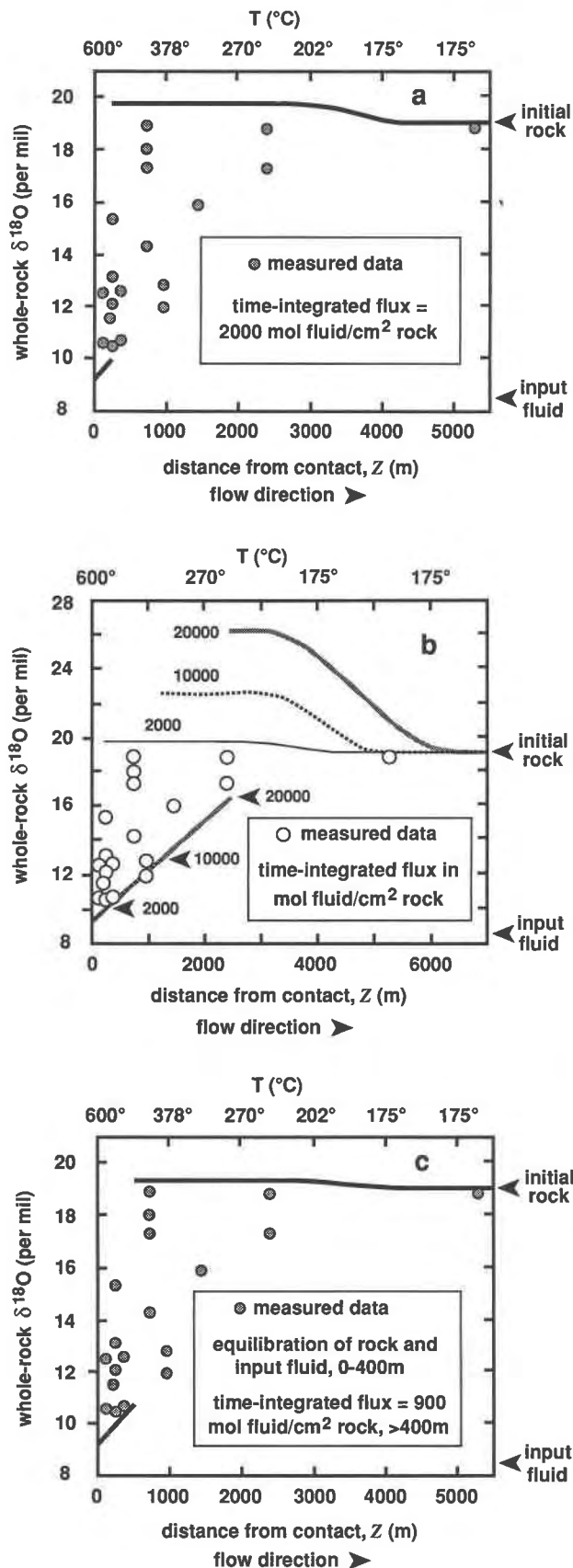
The best fit to the observed positions of the isograds occurs for $q_m \approx 2 \cdot 10^4$ mol/cm². The total calculated internal production of volatiles at distances greater than the position where quartz is exhausted is ≤ 3 mol% of this time-integrated flux; internal production of volatiles therefore was ignored in calculating the positions of the isograds.

Equation 2 can be used to predict not only the prograde reactions and positions of isograds in the model flow system but also reaction progress and hence the mode of model argillite at each point Z. The changes in modes as a function of Z for the case of $q_m = 2 \cdot 10^4$ mol/cm², for example, are illustrated in Figure 5. There is a gradual increase in the amount of diopside and a gradual decrease in the amount of tremolite with Z in the diopside zone. In contrast, the amount of grossular and wollastonite in model argillite increases rapidly at values of Z less than those at which the two minerals first appear. The modes for $T < 350$ °C are only approximate, however, because they were computed from the equation for $T-X_{CO_2}$ conditions of the diopside-forming reaction in Table 2 extrapolated beyond its limit.

Metamorphism with fluid flow in the direction of decreasing temperature

A third set of models considers flow of fluid away from the Notch Peak pluton during contact metamorphism in the direction of decreasing temperature. One case considers flow of magmatic fluid outward from the pluton-metasediment contact and a range of likely time-integrated fluxes. A second case attempts to predict the mineralogical and isotopic consequences of the physical model for fluid flow in the aureole proposed by Labotka et al. (1988a). In both cases considered, the spatial coordinate z in Equation 1 is parallel to and numerically identical to distance Z measured from the pluton-metasediment contact.

Coupled fluid flow and isotopic reaction. Prior to fluid flow argillite is considered to contain initially a small porosity filled with H₂O fluid in isotopic exchange equilibrium with calcite rock of $\delta^{18}O = +19\%$. Temperature is defined along the direction of flow by the equation in Table 2. The chemical and isotopic composition of fluid emanating from the pluton is pure H₂O and $\delta^{18}O = +8.5\%$ (Nabelek et al., 1984). In the first case considered, fluid simply flows out of the pluton into the argillite. Given the radius of the Notch Peak pluton (8 km) and the probable H₂O content of the parent magma (3%), both from Labotka et al. (1988a), the maximum time-integrated magmatic fluid flux that could have flowed horizontally into the aureole from the pluton may be computed. Assuming densities of magma and fluid equal to 2.5 and 1 g/cm³, respectively, the time-integrated mole flux, $q_m =$



1667 mol/cm². Unless there was significant focusing of fluid flow, the range in likely q_m values is ≈ 0 –2000 mol/cm².

After fluid flow commences, the O isotope alteration of rock as a function of z ($\equiv Z$) and T can be computed from Equation 1 for specified values of q_m . Results are illustrated in Figure 6a for the likely maximum $q_m = 2000$ mol/cm². Down-temperature flow and $q_m = 2000$ mol/cm² produce a discontinuity in whole-rock $\delta^{18}\text{O}$ of 9.7‰ at $Z = 246$ m, which represents the original discontinuity in isotopic composition of fluid at the contact swept downstream by flow. On the side of the discontinuity close to the pluton, rocks have $\delta^{18}\text{O} = 9.3$ –10.0‰ resulting from complete equilibration between argillite and magmatic fluid with $\delta^{18}\text{O} = +8.5$ ‰. On the other side of the discontinuity, rocks have $\delta^{18}\text{O}$ greater than the initial value (19.7‰). For values of $q_m < 2000$ mol/cm², the discontinuity retreats to distances < 246 m from the contact. The model therefore predicts that down-temperature flow of magmatic fluid produces ^{18}O depletion in argillites only within ≈ 246 m of the contact and (formally) no whole-rock isotopic compositions in the range 10–19‰. In nature, the computed discontinuity in Figure 6a would be smoothed slightly by diffusion and dispersion, and a continuous range of isotopic compositions would develop. The transition from low- $\delta^{18}\text{O}$ values to high- $\delta^{18}\text{O}$ values, however, would occur over a relatively small distance, and it would be unlikely that field studies would sample more than a few specimens precisely at the transition.

For completeness, Figure 6b illustrates predicted isotopic alteration that would result if down-temperature magmatic fluid flow were somehow focused and values of $q_m > 2000$ mol/cm² were attained. As time-integrated fluid flux increases, the region of ^{18}O -depleted rocks close to the pluton expands to larger values of Z . For all values of q_m , however, the 9.7‰ discontinuity is retained. Furthermore, for values of $q_m \geq 10^4$ mol/cm², significant ^{18}O

Fig. 6. Measured and calculated whole-rock O isotope compositions of calcareous argillites as a function of distance from the pluton-metasediment contact. Measured distance- $\delta^{18}\text{O}$ data same as in Figure 1. All calculations consider flow of magmatic H₂O fluid ($\delta^{18}\text{O} = 8.5$ ‰) in the direction of decreasing temperature. Temperatures calculated from equation for temperature profile in Table 2. (a) Predicted isotopic compositions for time-integrated flux of 2000 mol/cm² and flow from the pluton-metasediment contact (thick black curves). (b) Predicted isotopic compositions for time-integrated fluxes of 2000, 10000, and 20000 mol/cm² and flow from the pluton-metasediment contact. Curves for the three different fluxes superimpose along their positively inclined portions and along their horizontal portions that lie at 19‰. For each value of time-integrated flux, only that portion of the inclined line with positive slope between $Z = 0$ and the point indicated by the appropriately numbered arrow applies. (c) Predicted whole-rock isotopic compositions if argillite perfectly equilibrates with magmatic fluid at 0–400 m from the contact and if 900 mol/cm² H₂O fluid with $\delta^{18}\text{O} = 8.5$ ‰ flows down-temperature from a position at 400 m.

enrichment, $>2.5\%$, develops in the outer portion of the aureole. For time-integrated flux $\leq 2 \cdot 10^4$ mol/cm², even considering the effect of diffusion and dispersion in smoothing the discontinuity, all or almost all whole-rock $\delta^{18}\text{O}$ values of argillite should either lie along the inclined line between 9.3% at $Z = 0$ and $\delta^{18}\text{O} = 16.4\%$ at $Z = 2460$ m (corresponding to perfect equilibration of rock with magmatic fluid) or be $>19\%$ (Fig. 6b).

Labotka et al. (1988a) proposed perfect equilibration (by diffusion) of argillite with magmatic fluid in the innermost 400 m of the contact aureole and fluid flow away from the pluton with time-integrated fluxes in the range 800–1000 mol/cm² (p. 1321 of their article). A second case therefore considered the isotopic alteration caused by equilibration of argillite with fluid of $\delta^{18}\text{O} = 8.5\%$ at $Z = 0$ –400 m and flow of that same fluid ($q_m = 900$ mol/cm²) in the direction of decreasing temperature at $Z > 400$ m (computed with Eq. 1). Results are illustrated in Figure 6c. A discontinuity in whole-rock $\delta^{18}\text{O}$ is produced with one group of values 9.3–10.6‰ lying along the inclined line between $Z = 0$ and 511 m and a second group with uniform $\delta^{18}\text{O} = 19.3\%$ at $Z = 511$ –4000 m.

Coupled fluid flow and mineralogical reaction. The mineralogical effects of magmatic fluid flow in the direction of decreasing temperature were simulated by considering flow of pure H₂O fluid away from the pluton into the argillite. Prior to flow the mineral content of the argillite was considered to be that produced by heating the rock with a tiny porosity filled with CO₂-H₂O fluid to peak temperatures in the aureole (i.e., that developed along the thick gray shaded path in Fig. 3a). The infiltrating fluid is out of chemical equilibrium with the assemblage calcite + quartz + anorthite + diopside adjacent to the contact and will react with it. Reactions driven by infiltration of nonequilibrium fluids in rocks produce sharp reaction fronts that propagate downstream (Bickle and Baker, 1990b). For the case of a single decarbonation-dehydration reaction driven by the flow of H₂O fluid in the direction of decreasing temperature, the relation between the time-integrated mole fluid flux and the distance that the reaction front moves downstream from the inlet ($z = 0$) is

$$q_m = n_{\text{CO}_2} \int_0^z \frac{1}{X_{\text{CO}_2}(z)} dz - (n_{\text{CO}_2} + n_{\text{H}_2\text{O}})z \quad (3)$$

where $X_{\text{CO}_2}(z)$ is the functional dependence between X_{CO_2} of fluid in equilibrium with reactants and products and distance z along the flow path (computed from equations in Table 2), and n_{CO_2} and $n_{\text{H}_2\text{O}}$ are the moles CO₂ and H₂O, respectively, released by the reaction per cm³ rock (Ferry, 1991). For down-temperature magmatic fluid flow into the aureole, the spatial coordinate z in Equation 3 is parallel to and numerically identical to distance Z measured from the pluton-metasediment contact.

When more than one reaction front occurs along the flow path, however, there is no simple analytical expression that links time-integrated flux to progress of de-

volatilization reactions (except the reaction farthest upstream, whose position is specified by Eq. 3). A finite-element computer code therefore was written to predict the identity of reactions along the flow path and to calculate reaction progress as a function of q_m . The program specifically simulated fluid-rock interaction by dividing a 3-km column of argillite with 1-cm² cross-sectional area and $\approx 1\%$ fluid-filled porosity into 300 boxes. Temperatures at the ends of the column were 600 and 202 °C; a uniform temperature was assigned to each box based on the temperature at its midpoint defined by the equation in Table 2. An increment of H₂O fluid corresponding to the porosity of one box, Δq_m moles, was considered to enter the column at the high-temperature end. The increment of fluid displaced the fluid from each box to the next box immediately downstream. The displaced fluid either caused no reaction or drove one of the mineral-fluid reactions illustrated in Figure 3a. If reaction occurred, its progress was computed according to

$$X_{\text{CO}_2} = [(X_{\text{CO}_2}^0)(\Delta q_m) + \nu_{\text{CO}_2}\xi] / [\Delta q_m + (\nu_{\text{CO}_2} + \nu_{\text{H}_2\text{O}})\xi] \quad (4)$$

where $X_{\text{CO}_2}^0$ is the composition of fluid entering the box and X_{CO_2} is the composition of fluid after equilibrium is attained and reaction complete (see Ferry, 1986, 1989, or Bickle and Baker, 1990b, for further detail). Values of X_{CO_2} for each reaction at each temperature along the column were taken from equations in Table 2. A new increment of fluid was considered to enter the column and the calculation repeated until a desired time-integrated fluid flux had passed through the column. Results are summarized in Figure 7 and Table 1.

The first case considered was simply flow of H₂O fluid outward from the pluton-metasediment contact in the direction of decreasing temperature for a range of values of q_m (Fig. 7). For values of time-integrated flux >200 mol/cm², the initial assemblage close to the pluton, calcite + anorthite + quartz + diopside, reacts completely to calcite + diopside + grossular + wollastonite. With increasing distance (Z) from the contact, a sharp wollastonite reaction front is encountered across which the stable mineral assemblages changes to calcite + grossular + quartz + diopside. The position of the wollastonite front computed from the computer code (Eq. 4) agrees exactly with the position calculated analytically (Eq. 3). With further increasing Z a grossular reaction front occurs across which the stable assemblage changes to calcite + anorthite + quartz + diopside. At still greater Z a diopside reaction front occurs across which the assemblage changes to calcite + anorthite + quartz + tremolite. The reaction fronts migrate outward from the pluton-metasediment contact as a function of time-integrated fluid flux (Fig. 7). Regardless of time-integrated flux, tremolite + calcite + quartz + diopside coexist only across the sharp interface corresponding to the diopside reaction front.

A second case simulated mineralogical consequences of the flow model of Labotka et al. (1988a) by considering that argillite first fully equilibrates with magmatic fluid (pure H₂O) in the innermost 400 m of the contact aureole.

Rock therefore is composed of calcite + diopside + grossular + wollastonite prior to fluid flow at $Z < 400$ m and calcite + quartz + anorthite + tremolite + trace diopside farther away from the pluton. A time-integrated flux of 900 mol/cm^2 H_2O fluid then flows outward from a position at $Z = 400$ m. Computations were the same as before but with a smaller (1 m) box size; results are listed in Table 1. After flow is complete, calcite + quartz + anorthite + tremolite have reacted completely to calcite + diopside + grossular + wollastonite between $Z = 400$ and 417 m. At a sharp interface within the box at 417–418 m, calcite + diopside + grossular + wollastonite + quartz coexist. Between $Z = 418$ and 428 m calcite + quartz + anorthite + tremolite have reacted completely to calcite + diopside + grossular + quartz. At a sharp interface within the box at 428–429 m, calcite + diopside + grossular + anorthite + quartz coexist. Between $Z = 429$ and 588 m calcite + quartz + anorthite + tremolite have reacted completely to calcite + diopside + anorthite + quartz. At a sharp interface within the box at 588–589 m, calcite + diopside + anorthite + quartz + tremolite coexist. At $Z > 589$ m calcite + anorthite + quartz + tremolite remain. After flow is complete the initial stable coexistence of calcite + quartz + anorthite + tremolite + diopside does not occur over a distance interval but is limited to a sharp interface in the single box at $Z = 588$ –589 m.

DISCUSSION

Choice of preferred model of fluid-rock interaction during contact metamorphism in the Notch Peak aureole

Table 1 summarizes the isotopic and mineralogical consequences of the different models of contact metamorphic fluid-rock interaction considered in this study. Comparison of calculated isotopic compositions and positions of isograds with observed values leads to the choice of a preferred model for metamorphism in the Notch Peak aureole. Models of contact metamorphism that do not involve fluid flow can be summarily dismissed. Such models fail to produce either grossular or wollastonite and predict virtually no change in whole-rock O isotope compositions during metamorphism.

Models that involve flow of magmatic fluid outward from the pluton in the direction of decreasing temperature reproduce all observed isograds in the proper order and maximum whole-rock ^{18}O depletions of the correct magnitude, $\approx 10\text{‰}$ $\delta^{18}\text{O}$. For the range of q_m in Figure 7, 0 – $3.5 \cdot 10^4 \text{ mol/cm}^2$, these models, however, predict a diopside isograd that is much closer to the pluton than observed ($Z < 900$ m). For the range of likely q_m , 0 – 2000 mol/cm^2 , the position of the model diopside isograd lies even closer, < 590 m, and the predicted positions of the grossular and wollastonite isograds are also closer to the pluton than observed (Fig. 7; Table 1). Both models of down-temperature flow predict a sharp spatial separation of reactants and products of the wollastonite-, grossular-, and diopside-forming reactions. In the case of the wol-

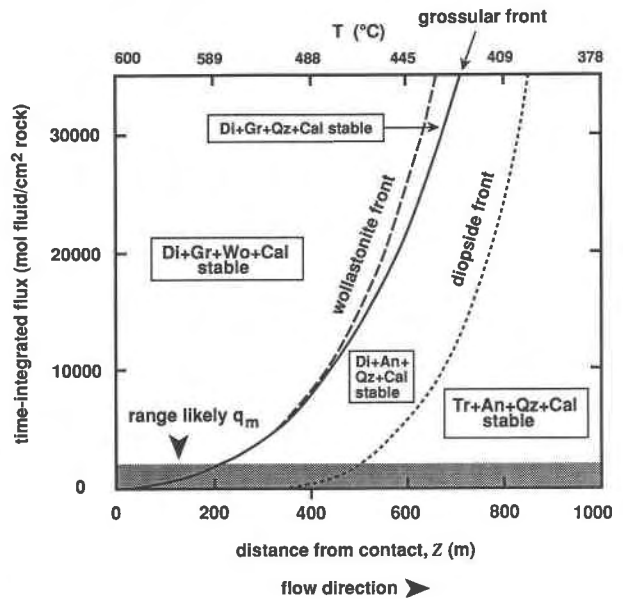


Fig. 7. Positions of reaction fronts calculated from Equations 3 and 4 as a function of time-integrated H_2O fluid flux flowing in the direction of decreasing temperature from the pluton-metasediment contact (see text for details). Mineral abbreviations as in caption to Figure 2. With increasing distance from the contact, the disappearance of wollastonite exactly coincides with the appearance of quartz, disappearance of grossular coincides with the appearance of anorthite, and disappearance of diopside coincides with the appearance of tremolite. Temperatures calculated from the equation for temperature profile in Table 2.

lastonite- and grossular-forming reactions, the predicted reaction fronts are neither confirmed nor refuted by observed field relations (Labotka et al., 1988a, their Table 1). In the case of the diopside-forming reaction, however, the predicted reaction front deviates greatly from the observed coexistence of tremolite + calcite + quartz + diopside in the field over a distance of at least 720 m perpendicular to the pluton-metasediment contact.

Models of down-temperature flow predict a bimodal distribution of whole-rock O isotopic compositions of argillite in the contact aureole unlike the continuous range of values observed. The models further predict a narrow range of whole-rock $\delta^{18}\text{O}$ values close to the pluton. For example, models that involve equilibration of argillite with magmatic fluid in the innermost 400 m of the aureole predict a range of whole-rock $\delta^{18}\text{O}$ 1‰ or less. Contrary to prediction, the observed range is $\approx 5\text{‰}$ (Figs. 2, 6; Nabelek et al., 1984; Labotka et al., 1988a). Furthermore, regardless of the value of time-integrated fluid flux and giving consideration to the effect of diffusion in smoothing predicted discontinuities, down-temperature flow fails to explain why most observed whole-rock isotopic compositions occur in the region of Figure 6b between the inclined line (perfect equilibration between argillite and magmatic fluid) and the initial isotopic

composition of the rock (19‰). Models of contact metamorphism that involve fluid flow in the direction of decreasing temperature qualitatively explain the first-order isotopic and mineralogical features of the Notch Peak aureole but provide an unsatisfactory quantitative explanation of the spatial distribution of both whole-rock isotopic compositions and of mineral reactants and products within the aureole.

The model that involves flow of fluid inward toward the pluton in the direction of increasing temperature also reproduces all observed isograds in the proper order and maximum whole-rock ^{18}O depletions of the correct magnitude, $\approx 9\%$ $\delta^{18}\text{O}$. Moreover, for time-integrated fluxes in the range $(1.5\text{--}2.5) \cdot 10^4$ mol/cm 2 , the predicted positions of all isograds match observed positions in the field. The model of up-temperature flow predicts coexistence of reactants and products of the wollastonite-, grossular-, and diopside-forming reactions over a range of distance in the field. The predicted narrow range of coexistence of reactants + products of the wollastonite- and grossular-forming reactions (0.1–0.3 km) is consistent with, but not confirmed by, observed relations in the field (Labotka et al., 1988a, their Table 1). In the case of the diopside-forming reaction, the predicted coexistence of tremolite + calcite + quartz + diopside in the field over a distance of $\approx 1\text{--}2$ km is consistent with the observed coexistence over a distance of at least 0.7 km but not more than 2.1 km.

Given the range in values of q_m , $(1.5\text{--}2.5) \cdot 10^4$ mol/cm 2 , the model for fluid flow in the direction of increasing temperature reproduces 70% of the measured whole-rock isotopic compositions to within $\approx 1\%$ $\delta^{18}\text{O}$ (open circles, Fig. 2). The remaining 30% of the values could be plausibly explained if less altered argillites were less permeable by a factor of 10. Models of contact metamorphism that involve fluid flow in the direction of increasing temperature explain the first-order isotopic and mineralogical features of the Notch Peak aureole both qualitatively and quantitatively and are preferred over models of metamorphism that either do not involve fluid flow or involve flow in the direction of decreasing temperature.

Discussion of preferred model

The numerical simulation of fluid flow, mineral reaction, and isotopic alteration during contact metamorphism in the Notch Peak aureole indicates that both the mineral reactions and isotopic shifts can be produced by flow of $\approx 2 \cdot 10^4$ mol/cm 2 fluid through the contact aureole in an up-temperature direction. Uncertainties in this value may be evaluated from Figures 2 and 4. If q_m were $< 1 \cdot 10^4$ mol/cm 2 , (1) maximum predicted whole-rock O isotopic shifts would be $\leq 4\%$, less than observed, and (2) quartz-free argillite would not extend further outward from the contact than $Z = 300$ m, less than generally observed. If $q_m \geq 3 \cdot 10^4$ mol/cm 2 , (1) predicted isotopic shifts within 0.5 km of the contact would all be $\geq 10\%$, greater than generally observed, and (2) the tremolite-out

isograd would lie further outward from the contact than 1.2 km, greater than generally observed.

The up-temperature flow direction is consistent with numerical simulations of pluton-driven hydrothermal systems (e.g., Norton and Knight, 1977; Norton and Taylor, 1979). The magnitude of the time-integrated mass flux ($\approx 3.6 \cdot 10^5$ g/cm 2) is similar to or slightly lower than values predicted for the Skaergaard hydrothermal system (Norton and Taylor, 1979). Because the Notch Peak stock has a "normal" igneous whole-rock $\delta^{18}\text{O} = 8.5\%$ (Nabelek et al., 1986), metamorphic fluids probably did not penetrate the stock but may have flowed vertically out of the aureole along the pluton-metasediment contact.

The preferred model for contact metamorphism in the Notch Peak aureole predicts formation of calc-silicate minerals at $\approx 300\text{--}450$ °C in equilibrium with $\text{CO}_2\text{--H}_2\text{O}$ fluids of very low X_{CO_2} . Although these temperatures are lower than normally associated with prograde metamorphic mineral reaction, they are in the same range of temperature at which diopside, calcium garnet, and wollastonite develop during calc-silicate mineralization in geothermal systems such as Cerro Prieto and Salton Sea (Bird et al., 1984; Schiffman et al., 1984). Furthermore, the aqueous fluids associated with the mineralization are characterized by very low f_{CO_2} (Bird and Norton, 1981). The inferred $T\text{--}X_{\text{CO}_2}$ conditions for metamorphism in the Notch Peak aureole therefore are not unreasonable and may in fact have a modern analogue in active geothermal systems.

The preferred model of fluid flow in the direction of increasing temperature produces metamorphosed argillite with mineralogical and isotopic composition at or close to equilibrium with magmatic fluid at $Z < \approx 300\text{--}500$ m (Table 1). The preferred model therefore does not rule out the possibility of chemical exchange between argillite and magmatic fluids in the innermost part of the contact aureole. If interaction between argillite and magmatic fluid did occur, it would not leave a mineralogical or isotopic record significantly different from that produced by inward, up-temperature flow of fluids alone.

Calculated results based on the model for fluid flow in the direction of increasing temperature (Table 1; Figs. 2, 4) are predicated on a number of assumptions: local mineral-fluid equilibrium, negligible mass transfer by diffusion and dispersion, one-dimensional flow, and a steady-state temperature profile along the flow path. Measured rates of hydrothermal reactions, observed mineral-fluid equilibrium in active geothermal fields, and fluid inclusion studies of metamorphic rocks all suggest that local mineral-fluid equilibrium is probably attained or nearly so during prograde metamorphism (see Baumgartner and Ferry, 1991, or Ferry, 1991, for further discussion).

The assumption of negligible mass transfer by diffusion (used to derive Eqs. 1–3) may be quantitatively evaluated. For an order-of-magnitude estimate of the lifetime of the hydrothermal event $\approx 5 \cdot 10^4$ yr (cf. Norton and Knight, 1977; Labotka et al., 1988a), the average flux

through the aureole was $\approx 3\text{--}4 \cdot 10^{-9} \text{ m}^3/\text{m}^2\text{-s}$. Considering the spatial scale of the aureole (1–10 km), the contact metamorphic event in the Notch Peak aureole plots within the field on Figure 6 of Bickle and McKenzie (1987) in which mass transfer by advection dominates over mass transfer by diffusion. The assumption used in the simulations therefore appears justified.

Metamorphic fluid flow was radial to the Notch Peak pluton. Radial flow causes time-integrated fluid flux to increase (up- T flow) or decrease (down- T flow) along the flow path. The calculated positions of isograds that depend on time-integrated flux (Figs. 4, 7) and predicted isotopic alteration associated with plausible models for down-temperature fluid flow (Fig. 6) all occur within 1 km of the contact. Given the inferred 8-km radius of the Notch Peak pluton (Labotka et al., 1988a, their Table 6), subhorizontal radial flow results in changes of time-integrated flux less than 15% within 1 km of the pluton-metasediment contact. Most isotopic alteration predicted by the preferred model for metamorphic fluid flow occurs within ≈ 2 km of the contact. Changes in time-integrated flux caused by radial flow are 20–25% within 2 km of the contact. In the specific case of the Notch Peak aureole, calculated results based on one-dimensional flow therefore are a good approximation of results based on radial flow (had they been computed).

The assumption of a steady-state temperature profile along the flow path was adopted because there is no simple, general, analytical solution to the coupling of fluid flow with chemical reactions when temperature changes during flow. In real contact aureoles temperature changes with time. Heat conduction tends to dampen initially large temperature gradients. Within the context of the preferred model of fluid flow [Darcy flux = $(3\text{--}4) \cdot 10^{-9} \text{ m/s}$], the scale of flow (1–10 km), and a likely value for thermal diffusivity of rock ($10^{-6} \text{ m}^2/\text{s}$), the thermal Peclet number is 3–40 (Bickle and McKenzie, 1987). Metamorphic fluid flow in the model therefore is a significant transport agent for heat. (The actual thermal effect of fluid flow, however, would be lessened somewhat by heat conduction from argillite to interbedded, impermeable limestone.) Specifically, up-temperature fluid flow steepens temperature gradients around the pluton relative to those produced by conduction alone (cf. Figs. 9 and 17 of Norton and Taylor, 1979). The effects of conduction and up-temperature fluid flow therefore tend to offset each other and will act to stabilize temperature gradients. Furthermore, a steady-state profile based on peak temperatures has a gentler slope than the real profile at the early stages of the metamorphic event and a steeper slope than the one at later stages. The profile of peak temperatures may be an adequate time-averaged profile of the entire event. Adoption of the steady-state temperature profile in Table 2 as a first approximation therefore is not wholly without justification.

Perhaps the best argument for assuming a steady-state temperature profile along the flow path is the success of

the preferred model in reproducing the first-order petrologic and isotopic features of the Notch Peak aureole (Figs. 2, 4). Nevertheless, the assumption is an obvious oversimplification. Because the real temperature profile during contact metamorphism evolved from one steeper than that in Table 2 to one gentler, however, it is difficult to predict how calculated results would change if a time-varying temperature profile were explicitly considered. An obvious future refinement of our simple models of contact metamorphism will be rigorous consideration of coupled fluid flow and the thermal evolution of aureoles.

Model of fluid-rock interaction proposed by Labotka et al. (1988a)

Two results from the simulations of contact metamorphism constitute critical evidence against the model for fluid-rock interaction in the Notch Peak aureole proposed by Labotka et al. (1988a). First, their postulated flow of H_2O fluid in the direction of decreasing temperature would produce a sharp transition between diopside-bearing rocks close to the pluton and tremolite-bearing rocks farther away. The prediction is independent of the exact values considered for the temperature profile and time-integrated flux. Such a sharp transition is inconsistent with the observed coexistence of diopside + tremolite + calcite + quartz over distances of $\approx 1\text{--}2$ km measured radially from the pluton-metasediment contact. Second, flow of $\approx 900 \text{ mol H}_2\text{O fluid/cm}^2 \text{ rock}$ with $\delta^{18}\text{O} \approx 8.5\text{‰}$ in the direction of decreasing temperature into argillite with initial $\delta^{18}\text{O} \approx 19\text{‰}$ would produce a bimodal distribution of whole-rock isotopic compositions with few or no compositions represented in the interval $\approx 11\text{--}19\text{‰}$. Such a gap in O isotopic compositions is inconsistent with numerous measured compositions in the range 11–19‰. Considering the mineralogical and isotopic consequences of this model, outward and down-temperature flow of magmatic fluid at distances $> \approx 400 \text{ m}$ from the pluton-metasediment contact is unlikely.

A second aspect of their model, significant mass transfer by diffusion over distances of $\approx 400 \text{ m}$ during the metamorphic event, may be evaluated both by examining current knowledge of diffusion coefficients and rock porosity during metamorphism and by observed field relations in the aureole. The characteristic distance, x , over which mass transfer occurs by diffusion in a fluid-saturated porous medium is

$$x \approx \sqrt{(\beta)(D_f)(t)} \quad (5)$$

where β is porosity, D_f is the coefficient of diffusion in the fluid, and t is the duration of mass transfer (Putnis and McConnell, 1980; Bickle and McKenzie, 1987). The duration of contact metamorphism (t) in the Notch Peak contact aureole was $\approx 5 \cdot 10^4 \text{ yr}$ (Labotka et al., 1988a). Three recent studies have reviewed the value of D_f at the conditions of metamorphism, and all recommend a value of $10^{-8} \text{ m}^2/\text{s}$ (Walther and Christ, 1984; Bickle and McKenzie, 1987; Hacker and Christie, 1991). Published

TABLE 3. Characteristic diffusion distances in $5 \cdot 10^4$ yr

D_r (m^2/s)	Porosity	Distance (m)
10^{-8}	$1 \cdot 10^{-8}$	0.1
10^{-8}	$5 \cdot 10^{-4}$	2.8
10^{-8}	$1 \cdot 10^{-2}$	13
10^{-7}	$1 \cdot 10^{-2}$	40
10^{-7}	0.25	199

estimates of in situ rock porosity during metamorphism are in the range 10^{-6} to $5 \cdot 10^{-4}$ (Bickle and Baker, 1990a; Ferry and Dipple, 1991). These values imply that $(\beta \cdot D_r)$ is in the range 10^{-14} to $5 \cdot 10^{-12}$ m^2/s and that mass transfer by diffusion was effective over distances of no more than 0.1–3 m during metamorphism in the Notch Peak aureole (Table 3). Even if porosity were 1%, diffusion distances would be no more than 13 m if $D_r = 10^{-8}$ m^2/s . Other estimates of $(\beta \cdot D_r)$, $(2-5) \cdot 10^{-15}$ m^2/s by Baumgartner and Valley (1991) and $\leq 10^{-15}$ m^2/s for 100 μm grains by Brady (1983), predict still smaller diffusion distances. Diffusion over distances on the order of 200 m can only occur in $5 \cdot 10^4$ yr if, as Labotka et al. (1988a) suggested, porosity is $\approx 25\%$ and D_r is $\approx 10^{-7}$ m^2/s (see Table 3). These values for both β and D_r are larger than those estimated by other published studies. Furthermore, a porosity of 25% is likely unstable at the conditions of metamorphism and would disappear by compaction on a time scale of ≈ 200 yr (Bickle and Baker, 1990b).

Contact metamorphism of siliceous limestones in the Notch Peak aureole provides an independent evaluation of the efficacy of mass transfer by diffusion during the metamorphic event. Contact metamorphosed limestones close to the pluton are ≈ 10 m thick, contain mineral assemblages that record equilibrium with fluid of X_{CO_2} as high as 0.8 (Hover-Granath et al., 1983), and have pristine and unaltered O isotope compositions (Nabelek et al. 1984). Limestones are interbedded with argillites that contain mineral assemblages which record $X_{CO_2} < 0.1$ (Hover-Granath et al., 1983; Labotka et al., 1988a). The argillites exhibit ^{18}O depletions of up to 10‰ caused by metamorphic fluid-rock interaction (Nabelek et al., 1984). If significant mass transfer by diffusion between pluton and metasediment caused the ^{18}O depletion and the low X_{CO_2} conditions of metamorphism in the argillites, then it is unclear why diffusion did not have a corresponding effect on the interbedded 10-m-thick limestone layers. Even if the porosity of the limestones was much less than the argillites (e.g., 1%), limestones should have thoroughly equilibrated by diffusion with fluids in the argillites for a value of $D_r \approx 10^{-7}$ m^2/s (Table 3). In fact, the unaltered O isotopic composition of the limestones and the high values of X_{CO_2} that minerals in them record are most consistent with $D_r \approx 10^{-8}$ m^2/s , $\beta \approx 10^{-6}$ (Table 3).

Consideration of current estimates of in situ porosity and D_r during metamorphism and of the mineral content and O isotopic composition of limestones interbedded with argillites in the Notch Peak aureole suggest that mass transfer by diffusion was unimportant during the contact

metamorphic event at scales > 1 m. Judging from Table 3, however, the critical factor in determining the characteristic diffusion distance during metamorphism is porosity (β). Future work on in situ metamorphic porosity will better resolve whether diffusion in contact aureoles is an effective mechanism for mass transfer over distances of less than a few meters or over distances of hundreds of meters.

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