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On the $^{18}\text{O}/^{16}\text{O}$ record of reaction progress in open and closed metamorphic systems

Edward D. Young

Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road NW, Washington, D.C. 20015-1305, USA

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ABSTRACT

A general formalism is described for predicting shifts in mineral $^{18}\text{O}/^{16}\text{O}$ attending changes in intensive and extensive thermochemical parameters during metamorphism. The method involves solving simultaneously linear differential equations describing changes in $\delta^{18}\text{O}$ with requisite mass balance and thermodynamic equations and can be modified to accommodate a variety of open and closed-system conditions. Analytical solutions for $\delta^{18}\text{O}$ as a function of reaction progress (ξ) are presented for simple systems experiencing closed-system evolution, Rayleigh dehydration, and fluid infiltration. An example application involving $\delta^{18}\text{O}$ zoning in garnet illustrates that comparisons of predicted covariations among $\delta^{18}\text{O}$ values, cation concentrations, and mineral abundances to patterns preserved in natural rocks can be used to reconstruct metamorphic net-transfer reaction histories. Such comparisons also provide new tests useful for determining the relative importance of other processes, such as Ostwald ripening, during the textural evolution of metamorphic rocks. The presented methodology constitutes the necessary framework for evaluating small-scale variations in $\delta^{18}\text{O}$ in the context of parageneses in metamorphic rocks.

“... the number of conditions necessary for equilibrium, will be diminished, in a case otherwise the same, as the number of equations of conditions is increased”

—Gibbs, 1876

1. Introduction

Variations in $^{18}\text{O}/^{16}\text{O}$ of a given mineral species within a metamorphic terrane are often attributed to changes in temperature (T), bulk composition, or degree of fluid interaction [1]. However, any factor which governs the state of a rock system can in principle affect changes in mineral $^{18}\text{O}/^{16}\text{O}$ as a result of ensuing reactions which cause changes in mineral proportions (net-transfer reactions). Many existing formalisms for interpreting mineral oxygen isotope ratios in rocks do not consider these effects [e.g. 2] and are therefore of limited use in metamorphic studies. Advances in laser-heating methods for *in-situ* mineral isotope ratio measurements [3,4,5] provide the impetus for more rigorous investigations of the extent to which variations in mineral $^{18}\text{O}/^{16}\text{O}$ can be attributed to progress of net-transfer reactions during metamorphism.

Previous studies [6,7] used mass balance constraints combined with numerical calculations to demonstrate that a complete and accurate understanding of reaction history is often necessary for correct interpretation of variations in metamorphic mineral oxygen isotope ratios. Until now, however, there has been no formal approach for relating variations in mineral $^{18}\text{O}/^{16}\text{O}$ to changes in other chemical parameters during evolution of metamorphic systems [8]. Of particular importance are covariations among $^{18}\text{O}/^{16}\text{O}$ and mineral cation concentrations. Such covariations are inevitable consequences of continuous net-transfer reactions and comprise potentially powerful tools for deciphering metamorphic reaction histories.

In this paper the inverse problem of using mineral oxygen isotope ratios to elucidate the nature of net-transfer reactions during metamorphism is addressed. A method is described for relating changes in

extensive and intensive thermodynamic parameters to $\delta^{18}\text{O}_i$ (the permil difference in $^{18}\text{O}/^{16}\text{O}$ between a mineral or fluid phase i and a standard). The method builds on the differential thermodynamic formalism of Rumble [9] and Spear et al. [10] and the analysis of isotope variations in metamorphic systems presented by Rumble [6]. The equations are based on requisites for local equilibrium and consequently do not include space coordinates or the time variable. One can foresee, however, applications in diffusion and advective transport calculations where boundary and initial conditions are dictated by equilibrium states. No claim is made that the rigorous treatment presented here is mandatory for interpretation of oxygen isotope data in all metamorphic rocks. Indeed, in many instances shifts in mineral $\delta^{18}\text{O}$ values attributable to reactions are below detection limits with current technology. Rather, attention is drawn to the formal link between mineral $\delta^{18}\text{O}$ values and other chemical parameters to demonstrate that measurable correlations among these quantities can be useful and are expected in some metamorphic rocks.

Explicit solutions to the equations comprising the method are presented for several simple examples. It is hoped that demonstration of analytical solubility for a variety of problems will reinforce to the reader not only the validity of the approach, but also its broad applicability.

2. Theory

Spear [11] and Young [12] showed that the concept of reaction progress can be incorporated into a system of linear differential thermodynamic equations depicting heterogeneous equilibria along quasi-statal equilibrium paths. The resulting sets of equations comprise a general approach for relating changes in modal abundances of mineral phases to changes in factors of state which govern open or closed thermodynamic systems. This methodology can be extended to include equations which describe changes in mineral isotope ratios (in the standard δ notation) during metamorphism.

In order to simplify the presentation of systems of equations, use is made of the indicial notation and the Einstein summing convention prevalent in mechanics and other fields. With this convention, an index which appears twice in a term represents a summation over the range of the index. The summation convention is suspended in favor of explicit summation symbols where potential ambiguities arise from application of the former (the summing convention is not used in equations where explicit summation symbols appear).

2.1 Thermodynamic formalism

The thermodynamic formalism used in this paper is described in detail elsewhere [13]. The equations are presented here to illustrate compatibility with the isotope equations introduced later. Only those systems in which H_2O is the sole fluid species are considered explicitly. Extensions to systems which include multicomponent fluids are described or are self evident.

For each of the linearly independent reactions r among phase components i in a heterogeneous system, the condition for equilibrium is [14]

$$0 = \sum_i \nu_{ir} \mu_i \quad (1)$$

where μ_i is the chemical potential of species i and ν_{ir} is the stoichiometric coefficient for species i in reaction r . Equation (1) in indicial notation becomes

$$0 = \nu_{ir} \mu_i \quad (1a)$$

where the summation over i is implied. The differential form of the equilibrium condition is then

$$0 = \frac{\partial(\nu_{ir} \mu_i)}{\partial T} dT + \frac{\partial(\nu_{ir} \mu_i)}{\partial P} dP + \frac{\partial(\nu_{ir} \mu_i)}{\partial x_j} dx_j \quad (2)$$

where T is temperature, P is pressure, and x_j is the mole fraction of phase component j in the appropriate host phase. Coefficients in eq. (2) are evaluated as follows:

$$\frac{\partial(\nu_{ir}\mu_i)}{\partial T} = \left(-\nu_{ir}\hat{S}_i^{1\text{bar},T*} + \nu_{sr}R \ln a_s + \nu_{\text{H}_2\text{O},r}R \ln f_{\text{H}_2\text{O}}^{P,T} + \nu_{\text{H}_2\text{O},r}RT \left(\frac{\partial \Gamma_{\text{H}_2\text{O}}^*}{\partial T} \right) \right) \quad (3)$$

$$\frac{\partial(\nu_{ir}\mu_i)}{\partial P} = (\nu_{sr}\hat{V}_s^{1\text{bar},298*}) \quad (4)$$

$$\frac{\partial(\nu_{ir}\mu_i)}{\partial x_j} = \sum_i \nu_{ir} \left(\frac{RT}{a_i} \frac{\partial a_i}{\partial x_j} \right) \quad (5)$$

In eqs. (3)–(5) s is the index for solid phase components, * denotes pure species, $\hat{S}_i^{1\text{bar},T*}$ is the molar entropy of pure species i at the indicated conditions, a_i is the activity of phase component i , $f_{\text{H}_2\text{O}}^{P,T}$ and $\Gamma_{\text{H}_2\text{O}}^*$ are respectively the fugacity and fugacity coefficient for H_2O , $\hat{V}_s^{1\text{bar},298*}$ represents the molar volume of species s , and R is the ideal gas constant. Mole fractions x_j are subject to the additional summing constraints:

$$0 = \sum_j dx_{jk} \quad (6)$$

imposed by stoichiometry for each of the phases k .

Equations (2) and (6) comprise the relations among intensive variables in the heterogeneous thermodynamic system. Accordingly, the reader may verify that the variance of any system of equations obtained by application of (2) and (6) is consistent with Gibbs' familiar phase rule. Extensive variables, including molar quantities of phases M_k and molar amounts of system components η_l^{sys} , are included by adding one mass balance equation for each of the C system components of the form

$$0 = \sum_k \left(\sum_j x_{jk} \epsilon_{jkl} \right) dM_k + \sum_k \sum_j (M_k \epsilon_{jkl}) dx_{jk} - d\eta_l^{\text{sys}} \quad (7)$$

where ϵ_{jkl} is the number of moles of system component l in phase component j . Equations (2), (6) and (7) represent a system of linear differential equations which can be solved simultaneously for changes in intensive and extensive variables in a heterogeneous thermodynamic system. The *total* variance of the system of equations is $C + 2$, as prescribed by macroscopic thermodynamics [14].

2.2 Isotope equations

Variations in mineral isotope ratios can be included in the thermodynamic analysis described above by addition of equations for the total differentials of $\delta^{18}\text{O}$ for each phase i :

$$d\delta^{18}\text{O}_i = \left(\frac{\partial \delta^{18}\text{O}_i}{\partial T} \right) dT + \sum_k \left(\frac{\partial \delta^{18}\text{O}_i}{\partial M_k} \right) dM_k + \sum_f \left(\frac{\partial \delta^{18}\text{O}_i}{\partial x_f} \right) dx_f + d\delta^{18}\text{O}_{\text{sys}} \quad (8)$$

where x_f represents the mole fraction of oxygen-bearing fluid species f in the fluid phase. The thermodynamic and isotope equations are linked by the variables dT , dM_k , and, in the general case of impure fluid, dx_f . Simultaneous solution of eq. (2), (6), (7) and (8) affords quantitative assessment of the dependence of $\delta^{18}\text{O}$ on macroscopic thermodynamic factors of state. Equation(s) (8) add one degree of freedom to the system. The increase in variance derives from the distinction between ¹⁸O and ¹⁶O, and is represented by the variable $\delta^{18}\text{O}_{\text{sys}}$. The total variance remains $C + 2$ despite the added degree of freedom as ¹⁸O is counted among the C system components. For example, the system components can be regarded as consisting of ¹⁸O together with oxides of general form $M_x^{16}\text{O}_y$.

Coefficients for eq. (8) are derived by differentiation of the expression

$$\delta^{18}\text{O}_i = \sum_s (\omega_s M_s / \tau) \Delta_{is}^T + \sum_f (x_f \omega_f M_{\text{fluid}} / \tau) \Delta_{if}^T + \delta^{18}\text{O}_{\text{sys}} \quad (9)$$

where ω_s and ω_f are oxygens per mole of solid phase s and fluid species f , respectively, τ is the total number of oxygens in the system, and Δ_{is}^T (Δ_{if}^T) is the temperature-dependent equilibrium difference in $\delta^{18}\text{O}$ between phase i and phase s (fluid species f) expressed as

$$\Delta_{is}^T \approx \frac{A_{is}}{T^2} + \frac{B_{is}}{T} + C_{is} \quad (10)$$

Equation (9) closely approximates a mass balance equation for ^{18}O [15]. The resulting coefficients are

$$\left(\frac{\partial \delta^{18}\text{O}_i}{\partial T} \right) = \sum_{s \neq i} \left(\frac{-2A_{is}\omega_s M_s}{\tau T^3} - \frac{B_{is}\omega_s M_s}{\tau T^2} \right) + \sum_f \left(\frac{-2A_{if}\omega_f x_f M_{\text{fluid}}}{\tau T^3} - \frac{B_{if}\omega_f x_f M_{\text{fluid}}}{\tau T^2} \right) \quad (11)$$

$$\left(\frac{\partial \delta^{18}\text{O}_i}{\partial M_k} \right) = \frac{\Delta_{ik}^T \omega_k}{\tau} - \frac{\omega_k (\sum_s \Delta_{is}^T \omega_s M_s + \sum_f \Delta_{if}^T \omega_f x_f M_{\text{fluid}})}{\tau^2} \quad (12)$$

$$\left(\frac{\partial \delta^{18}\text{O}_i}{\partial x_f} \right) = \frac{\Delta_{if}^T \omega_f M_{\text{fluid}} (\tau - \omega_f x_f M_{\text{fluid}})}{\tau^2} - \omega_f M_{\text{fluid}} \left(\frac{\sum_s \Delta_{is}^T \omega_s M_s + \sum_{f_j \neq f} \Delta_{if_j}^T \omega_{f_j} x_{f_j} M_{\text{fluid}}}{\tau^2} \right) \quad (13)$$

Simultaneous solution of eq. (2), (6), (7) and (8) can be performed numerically or, in some instances, analytically. The solutions permit calculation of shifts in mineral $\delta^{18}\text{O}$ associated with variations in mode, T , P , phase composition and fluid conditions. In many geologically realizable systems, including those closed to mass transfer, those experiencing fractional growth or resorption of minerals, and those open to infiltration of fluid of a prescribed composition, the total number of linearly independent *extensive* and *intensive* parameters is two (see examples below). The low total variance (not to be confused with the intensive variance prescribed by Gibbs' phase rule) results from incorporation of equations which govern the variations in extensive parameters for the particular process of interest. Consideration of extensive variables affords predictions of covariations among $\delta^{18}\text{O}$ and other measurable parameters such as phase chemical composition which cannot be obtained with analysis of intensive parameters alone. The cost of this low variance is a loss of generality. Predicted chemical and isotopic trends are only strictly applicable to systems of specified bulk composition and reaction history.

3. Example solutions

3.1 Closed-system reaction

Consider a rock composed of muscovite (Ms), quartz (Qtz), K-feldspar (Kfs), sillimanite (Sil) and water (H_2O) in the simplified system $\text{K}_2^{16}\text{O}-\text{Al}_2^{16}\text{O}_3-\text{Si}^{16}\text{O}_2-\text{H}_2^{16}\text{O}-^{18}\text{O}$. Among these pure phases, there is one linearly independent reaction in the case where the system is closed to transfer of mass:



Equations (2), (6), (7) and (8) evaluated in the context of this closed system (i.e. where $d\eta_l^{\text{sys}} = 0$ for all components l , $d\delta^{18}\text{O}_{\text{sys}} = 0$) yield a system of 10 equations in 12 variables. The total variance of the system is thus 2. Of these 2 independent parameters, no more than 1 may consist of an intensive variable as the intensive variance given by the phase rule is still 1. The 10 equations can be represented in indicial notation:

$$\frac{\partial \theta_i}{\partial \Lambda_j} d\Lambda_j = 0 \quad (14)$$

where the terms $\partial\theta_i/\partial\Lambda_j$ comprise the 10×12 coefficient matrix (Jacobian matrix) and $d\Lambda_j$ is the solution vector. In (14) θ_i represents the parameters ($\nu_j\mu_j, \eta_{K_2O}^{sys}, \eta_{Al_2O_3}^{sys}, \eta_{SiO_2}^{sys}, \eta_{H_2O}^{sys}, \delta^{18}O_{H_2O}, \delta^{18}O_{Sil}, \delta^{18}O_{Kfs}, \delta^{18}O_{Qtz}, \delta^{18}O_{Ms}$), Λ_j is the variable set ($T, P, M_{H_2O}, M_{Sil}, M_{Kfs}, M_{Qtz}, M_{Ms}, \delta^{18}O_{H_2O}, \delta^{18}O_{Sil}, \delta^{18}O_{Kfs}, \delta^{18}O_{Qtz}, \delta^{18}O_{Ms}$), and omission of subscripts for the partial derivatives indicates differentiation with respect to the denominator variable only.

Expressions for shifts in $\delta^{18}O$ with changes in M_{H_2O} at constant pressure ($dP = 0$), where M_{H_2O} is used to monitor the progress of reaction, can be obtained by subtracting terms for dM_{H_2O} from both sides of (14) and then dividing each equation by dM_{H_2O} . The resulting set of equations are of the form

$$\frac{\partial\theta_i}{\partial\Lambda'_j} \left(\frac{\partial\Lambda'_j}{\partial M_{H_2O}} \right)_P = - \frac{\partial\theta_i}{\partial M_{H_2O}} \tag{15}$$

where Λ'_j is equivalent to Λ_j with M_{H_2O} and P excluded and subscript P indicates that differentials refer to conditions of constant pressure. Premultiplication by the inverse of the Jacobian coefficient matrix $\partial\theta_i/\partial\Lambda'_j$ yields the solution for $(\partial\Lambda'_j/\partial M_{H_2O})_P$:

$$\left(\frac{\partial\Lambda'_j}{\partial M_{H_2O}} \right)_P = \begin{bmatrix} \left(\frac{\partial T}{\partial M_{H_2O}} \right)_P \\ \left(\frac{\partial M_{Sil}}{\partial M_{H_2O}} \right)_P \\ \left(\frac{\partial M_{Kfs}}{\partial M_{H_2O}} \right)_P \\ \left(\frac{\partial M_{Qtz}}{\partial M_{H_2O}} \right)_P \\ \left(\frac{\partial M_{Ms}}{\partial M_{H_2O}} \right)_P \\ \left(\frac{\partial \delta^{18}O_{H_2O}}{\partial M_{H_2O}} \right)_P \\ \left(\frac{\partial \delta^{18}O_{Sil}}{\partial M_{H_2O}} \right)_P \\ \left(\frac{\partial \delta^{18}O_{Kfs}}{\partial M_{H_2O}} \right)_P \\ \left(\frac{\partial \delta^{18}O_{Qtz}}{\partial M_{H_2O}} \right)_P \\ \left(\frac{\partial \delta^{18}O_{Ms}}{\partial M_{H_2O}} \right)_P \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \\ 1 \\ -1 \\ -1 \\ \nu_k \frac{\partial \delta^{18}O_{H_2O}}{\partial M_k} \\ \nu_k \frac{\partial \delta^{18}O_{Sil}}{\partial M_k} \\ \nu_k \frac{\partial \delta^{18}O_{Kfs}}{\partial M_k} \\ \nu_k \frac{\partial \delta^{18}O_{Qtz}}{\partial M_k} \\ \nu_k \frac{\partial \delta^{18}O_{Ms}}{\partial M_k} \end{bmatrix} \tag{16}$$

The summing convention is invoked over phases k for each element of solution vector (16). The first five elements of (16) are trivial, reflecting the fact that this system is univariant with respect to intensive parameters, and hence temperature cannot change at constant pressure, and the fact that changes in moles of phases are constrained by the stoichiometry of reaction (r1).

A comment on the relation between total variance and Gibbs' phase rule is warranted here. We have chosen as the 2 independent parameters P and $M_{\text{H}_2\text{O}}$, where the former is held constant and the latter is to be specified in order to determine the state of the system. Specification of 2 parameters was necessary in order to solve eq. (14). Gibbs' phase rule dictates that the system is "univariant". The univariant character of the system is manifest in (14) by the fact that holding more than 1 intensive variable constant, in this case both P and T , results in a singular Jacobian matrix (i.e. $|\partial\theta_i/\partial\Lambda_j| = 0$), making unique solution of (14) impossible. The method of calculation therefore includes an inherent check for violations of the phase rule in the form of the Jacobian. Clearly, however, Gibbs' phase rule cannot be interpreted as the total number of independent parameters. If such an interpretation were correct, solutions to (14) would be possible with specification of only 1 parameter. For example, holding P constant would be insufficient for solution of this 10×12 system of equations. This simple example illustrates the important distinction between *intensive* degrees of freedom given by the familiar phase rule, and total variance of the system which refers to the degrees of freedom among *both* intensive and extensive variables. The phase rule dictates the number of independent parameters which must be specified to establish the state of the system with regard to intensive parameters (e.g. T , P , phase composition), while the total variance gives the number of independent parameters required to establish the state of the system inclusive of extensive parameters (e.g. amounts of phases).

Inspection of eq. (10) shows that

$$\nu_k \frac{\partial \delta^{18}\text{O}_{\text{H}_2\text{O}}}{\partial M_k} = \nu_k \frac{\partial \delta^{18}\text{O}_{\text{Sil}}}{\partial M_k} = \nu_k \frac{\partial \delta^{18}\text{O}_{\text{Kfs}}}{\partial M_k} = \nu_k \frac{\partial \delta^{18}\text{O}_{\text{Qtz}}}{\partial M_k} = \nu_k \frac{\partial \delta^{18}\text{O}_{\text{Ms}}}{\partial M_k} \quad (17)$$

and therefore

$$\left(\frac{\partial \delta^{18}\text{O}_{\text{H}_2\text{O}}}{\partial M_{\text{H}_2\text{O}}} \right)_P = \left(\frac{\partial \delta^{18}\text{O}_{\text{Sil}}}{\partial M_{\text{H}_2\text{O}}} \right)_P = \left(\frac{\partial \delta^{18}\text{O}_{\text{Kfs}}}{\partial M_{\text{H}_2\text{O}}} \right)_P = \left(\frac{\partial \delta^{18}\text{O}_{\text{Qtz}}}{\partial M_{\text{H}_2\text{O}}} \right)_P = \left(\frac{\partial \delta^{18}\text{O}_{\text{Ms}}}{\partial M_{\text{H}_2\text{O}}} \right)_P \quad (18)$$

as required at constant temperature to preserve Δ_{ij}^T among the phases.

Substitution of eq. (12) into the solutions for $(\partial \delta^{18}\text{O}_i / \partial M_{\text{H}_2\text{O}})_P$ and replacement of $dM_{\text{H}_2\text{O}}$ with the forward reaction progress variable $d\xi$ (equivalency of $dM_{\text{H}_2\text{O}}$ and $d\xi$ can be deduced from the identity $M_k = M_k^\circ + \nu_k \xi$) affords the explicit functional relation between $d\delta^{18}\text{O}_i$ for phases i and reaction progress:

$$d\delta^{18}\text{O}_i = \sum_k \nu_k \omega_k \left[\frac{\Delta_{ik}}{\tau} - \sum_j \frac{(\omega_j \Delta_{ij} M_j)}{\tau^2} \right] d\xi \quad (19)$$

The analytical solution for $\delta^{18}\text{O}_i(\xi)$ is obtained by integration of (19):

$$\delta^{18}\text{O}_i = \delta^{18}\text{O}_i^\circ + \sum_k \nu_k \omega_k \left[\left(\frac{\Delta_{ik}}{\tau} - \sum_j \frac{\omega_j \Delta_{ij} M_j^\circ}{\tau^2} \right) \xi - \sum_j \frac{1}{2} \left(\frac{\nu_j \omega_j \Delta_{ij}}{\tau^2} \right) \xi^2 \right] \quad (20)$$

where $^\circ$ denotes initial values. Equation (20) demonstrates that mineral $\delta^{18}\text{O}$ values vary in an unambiguous manner with progress of closed-system net-transfer reactions even at constant temperature (and pressure) [cf. 16]. Shifts in $\delta^{18}\text{O}_i$ resulting from closed-system reactions are typically of the order of present-day limits of detection (several tenths of a permil). Nevertheless, the academic exercise of deriving eq. (20) elucidates the inexorable link between mineral $^{18}\text{O}/^{16}\text{O}$ and ξ and serves as preparation for establishing analogous relations in open systems where shifts in $\delta^{18}\text{O}_i$ values attending progress of reactions can be significantly larger.

3.2 Rayleigh distillation

Both the extensive amount of system components and the system ¹⁸O/¹⁶O are altered by fractional removal of a phase or phases. Perfect Rayleigh fractionation attending reaction can be described mathematically by addition of equations which prescribe the variations in η_i^{sys} and $\delta^{18}\text{O}_{\text{sys}}$ resulting from loss of the fractionating phases to the closed-system equations described above.

The equations which must be added in order to describe changes in η_i^{sys} during fractionation of phases F are of the form

$$0 = - \sum_F \frac{\partial \eta_i^{\text{sys}}}{\partial M_F} dM_F - \sum_F \sum_j \frac{\partial \eta_i^{\text{sys}}}{\partial x_{jF}} dx_{jF} - d\eta_i^{\text{sys}} \quad (21)$$

and are evaluated as follows (cf. eq. 7):

$$0 = - \sum_F \left(\sum_j x_{jF} \epsilon_{jFl} \right) dM_F - \sum_F \sum_j (M_F \epsilon_{jFl}) dx_{jF} - d\eta_i^{\text{sys}} \quad (22)$$

Addition of one equation of the form of (22) for each system component affected by fractionation to the closed-system equations is sufficient to model chemical changes during reactions involving Rayleigh fractionation or distillation. This can be seen by setting $d\eta_i^{\text{sys}}$ equal to 0 in (7), providing the closed-system equation for η_i^{sys} , and then adding the latter equation to (22), for which $d\eta_i^{\text{sys}}$ is not 0. The resultant expression is identical to (7) with the exception that the summations exclude fractionating phases (i.e. k in eq. (7) excludes F); i.e. fractionating phases do not contribute to the η_i^{sys} , which is a sufficient definition of perfect Rayleigh fractionation.

Changes in $\delta^{18}\text{O}_{\text{sys}}$ attending Rayleigh fractionation are described by the general expression

$$0 = - \sum_F \frac{\partial \delta^{18}\text{O}_{\text{sys}}}{\partial M_F} dM_F - \sum_F \frac{\partial \delta^{18}\text{O}_{\text{sys}}}{\partial \delta^{18}\text{O}_F} d\delta^{18}\text{O}_F - d\delta^{18}\text{O}_{\text{sys}} \quad (23)$$

The distinction between fluid species has been temporarily omitted in (23) for the sake of brevity. Equation (23) is evaluated by rearrangement and differentiation of (9):

$$0 = - \sum_F \frac{\omega_F}{\tau^2} \left(\sum_k \omega_k M_k \Delta_{Fk}^T \right) dM_F - \sum_F \frac{\omega_F M_F}{\tau} d\delta^{18}\text{O}_F - d\delta^{18}\text{O}_{\text{sys}} \quad (24)$$

Equation (24), when combined with eq. (8), in which $d\delta^{18}\text{O}_{\text{sys}}$ is set to 0, has the effect of removing the isotopic contribution of phases F from the system. Addition of (24) to the closed-system equations therefore can be used to calculate shifts in mineral $\delta^{18}\text{O}$ resulting from reactions involving Rayleigh fractionation or distillation.

Suppose now that as the phases Ms, Qtz, Kfs, Sil and H₂O react, H₂O produced by reaction (r1) is released from the system in a perfect Rayleigh distillation process. In this case, $d\eta_{\text{H}_2\text{O}}^{\text{sys}}$ and $d\delta^{18}\text{O}_{\text{sys}}$ are no longer 0 and they must be included in the system of equations. The stipulation that H₂O is lost from the system by the process of Rayleigh distillation allows one to write linear equations for both $d\eta_{\text{H}_2\text{O}}^{\text{sys}}$ and $d\delta^{18}\text{O}_{\text{sys}}$. In the case of the former, the appropriate equation is (22), which in the present example reduces to

$$0 = -dM_{\text{H}_2\text{O}} - d\eta_{\text{H}_2\text{O}}^{\text{sys}} \quad (25)$$

The expression for $d\delta^{18}\text{O}_{\text{sys}}$ derives from (24), which for this case yields

$$0 = - \frac{1}{\tau^2} \left(\sum_k \omega_k M_k \Delta_{\text{H}_2\text{O},k}^T \right) dM_{\text{H}_2\text{O}} - \frac{M_{\text{H}_2\text{O}}}{\tau} d\delta^{18}\text{O}_{\text{H}_2\text{O}} - d\delta^{18}\text{O}_{\text{sys}} \quad (26)$$

Equations (25) and (26) add two equations and two variables to the closed-system equations (14). The variance of the system of equations is hence unchanged. This is a general result applicable to systems in which variations in η_i^{sys} and $\delta^{18}\text{O}_{\text{sys}}$ are controlled by Rayleigh fractionation or distillation (i.e. eq. (22) and (24)).

Expressions for shifts in mineral $\delta^{18}\text{O}$ values with changes in $M_{\text{H}_2\text{O}}$ by the process of Rayleigh distillation at constant pressure, where again $M_{\text{H}_2\text{O}}$ is the monitor of progress of reaction (r1), are obtained by rearrangement of eq. (2), (6), (7), (8), (25) and (26) in the manner described for the closed-system example to produce the set of equations

$$\frac{\partial \theta'_i}{\partial \Lambda''_j} \left(\frac{\partial \Lambda''_j}{\partial M_{\text{H}_2\text{O}}} \right)_P = - \frac{\partial \theta'_i}{\partial M_{\text{H}_2\text{O}}} \quad (27)$$

where θ'_i represents the parameters ($\nu_j \mu_j$, $\eta_{\text{K}_2\text{O}}^{\text{sys}}$, $\eta_{\text{Al}_2\text{O}_3}^{\text{sys}}$, $\eta_{\text{SiO}_2}^{\text{sys}}$, $\eta_{\text{H}_2\text{O}}^{\text{sys}}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, $\delta^{18}\text{O}_{\text{Sil}}$, $\delta^{18}\text{O}_{\text{Kfs}}$, $\delta^{18}\text{O}_{\text{Qtz}}$, $\delta^{18}\text{O}_{\text{Ms}}$, $\eta_{\text{H}_2\text{O}}^{\text{sys}}$, $\delta^{18}\text{O}_{\text{sys}}$) and Λ''_j is the variable set (T , M_{Sil} , M_{Kfs} , M_{Qtz} , M_{Ms} , $\eta_{\text{H}_2\text{O}}^{\text{sys}}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, $\delta^{18}\text{O}_{\text{Sil}}$, $\delta^{18}\text{O}_{\text{Kfs}}$, $\delta^{18}\text{O}_{\text{Qtz}}$, $\delta^{18}\text{O}_{\text{Ms}}$, $\delta^{18}\text{O}_{\text{sys}}$). Notice that $(\partial \eta_{\text{H}_2\text{O}}^{\text{sys}} / \partial \Lambda''_j)$ and $(\partial \eta_{\text{H}_2\text{O}}^{\text{sys}} / \partial \Lambda''_j)$ are not equivalent, the former representing coefficients in (23) and the latter referring to coefficients in (7). Premultiplication by the inverse of the Jacobian matrix $\partial \theta'_i / \partial \Lambda''_j$ yields the solution for $(\partial \Lambda''_j / \partial M_{\text{H}_2\text{O}})_P$:

$$\begin{bmatrix} \left(\frac{\partial T}{\partial M_{\text{H}_2\text{O}}} \right)_P \\ \left(\frac{\partial M_{\text{Sil}}}{\partial M_{\text{H}_2\text{O}}} \right)_P \\ \left(\frac{\partial M_{\text{Kfs}}}{\partial M_{\text{H}_2\text{O}}} \right)_P \\ \left(\frac{\partial M_{\text{Qtz}}}{\partial M_{\text{H}_2\text{O}}} \right)_P \\ \left(\frac{\partial M_{\text{Ms}}}{\partial M_{\text{H}_2\text{O}}} \right)_P \\ \left(\frac{\partial \eta_{\text{H}_2\text{O}}^{\text{sys}}}{\partial M_{\text{H}_2\text{O}}} \right)_P \\ \left(\frac{\partial \delta^{18}\text{O}_{\text{H}_2\text{O}}}{\partial M_{\text{H}_2\text{O}}} \right)_P \\ \left(\frac{\partial \delta^{18}\text{O}_{\text{Sil}}}{\partial M_{\text{H}_2\text{O}}} \right)_P \\ \left(\frac{\partial \delta^{18}\text{O}_{\text{Kfs}}}{\partial M_{\text{H}_2\text{O}}} \right)_P \\ \left(\frac{\partial \delta^{18}\text{O}_{\text{Qtz}}}{\partial M_{\text{H}_2\text{O}}} \right)_P \\ \left(\frac{\partial \delta^{18}\text{O}_{\text{Ms}}}{\partial M_{\text{H}_2\text{O}}} \right)_P \\ \left(\frac{\partial \delta^{18}\text{O}_{\text{sys}}}{\partial M_{\text{H}_2\text{O}}} \right)_P \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \\ 1 \\ -1 \\ -1 \\ -1 \\ \frac{\nu_k (\partial \delta^{18}\text{O}_{\text{H}_2\text{O}} / \partial M_k) - (\partial \delta^{18}\text{O}_{\text{sys}} / \partial M_{\text{H}_2\text{O}})}{(\partial \delta^{18}\text{O}_{\text{sys}} / \partial \delta^{18}\text{O}_{\text{H}_2\text{O}}) + 1} \\ \frac{\nu_k (\partial \delta^{18}\text{O}_{\text{Sil}} / \partial M_k) - (\partial \delta^{18}\text{O}_{\text{sys}} / \partial M_{\text{H}_2\text{O}})}{(\partial \delta^{18}\text{O}_{\text{sys}} / \partial \delta^{18}\text{O}_{\text{H}_2\text{O}}) + 1} \\ \frac{\nu_k (\partial \delta^{18}\text{O}_{\text{Kfs}} / \partial M_k) - (\partial \delta^{18}\text{O}_{\text{sys}} / \partial M_{\text{H}_2\text{O}})}{(\partial \delta^{18}\text{O}_{\text{sys}} / \partial \delta^{18}\text{O}_{\text{H}_2\text{O}}) + 1} \\ \frac{\nu_k (\partial \delta^{18}\text{O}_{\text{Qtz}} / \partial M_k) - (\partial \delta^{18}\text{O}_{\text{sys}} / \partial M_{\text{H}_2\text{O}})}{(\partial \delta^{18}\text{O}_{\text{sys}} / \partial \delta^{18}\text{O}_{\text{H}_2\text{O}}) + 1} \\ \frac{\nu_k (\partial \delta^{18}\text{O}_{\text{Ms}} / \partial M_k) - (\partial \delta^{18}\text{O}_{\text{sys}} / \partial M_{\text{H}_2\text{O}})}{(\partial \delta^{18}\text{O}_{\text{sys}} / \partial \delta^{18}\text{O}_{\text{H}_2\text{O}}) + 1} \\ - \frac{(\partial \delta^{18}\text{O}_{\text{sys}} / \partial \delta^{18}\text{O}_{\text{H}_2\text{O}}) \nu_k (\partial \delta^{18}\text{O}_{\text{H}_2\text{O}} / \partial M_k) - (\partial \delta^{18}\text{O}_{\text{sys}} / \partial M_{\text{H}_2\text{O}})}{(\partial \delta^{18}\text{O}_{\text{sys}} / \partial \delta^{18}\text{O}_{\text{H}_2\text{O}}) + 1} \end{bmatrix} \quad (28)$$

where use is made of the summing convention over phases k . The first five elements of the solution vector are equivalent to the closed-system solutions and are intuitively obvious. The sixth element, $(\partial\eta_{\text{H}_2\text{O}}^{\text{sys}}/\partial M_{\text{H}_2\text{O}})_P = -1$, illustrates the essence of the Rayleigh dehydration process: for each mole of the phase H_2O produced by reaction (r1), the extensive amount of water in the system decreases by 1 mole.

Since eq. (17) is a general result, (18) also applies to solution (28) and $d\delta^{18}\text{O}$ for the phases are equivalent. With appropriate substitutions for $\partial\delta^{18}\text{O}_i/\partial M_k$ from (12), and for $\partial\delta^{18}\text{O}_{\text{sys}}/\partial M_{\text{H}_2\text{O}}$ and $\partial\delta^{18}\text{O}_{\text{sys}}/\partial\delta^{18}\text{O}_{\text{H}_2\text{O}}$ from (26) one obtains

$$d\delta^{18}\text{O}_i = \frac{\sum_k \nu_k \omega_k \left(\frac{\Delta_{ik}^T}{\tau} - \sum_j \frac{\omega_j \Delta_{ij}^T M_j}{\tau^2} \right) - \sum_j \frac{\omega_j \Delta_{\text{H}_2\text{O},j}^T M_j}{\tau^2}}{(M_{\text{H}_2\text{O}}/\tau) + 1} d\xi \quad (29)$$

The suitability of eq. (29) for describing the changes in mineral $\delta^{18}\text{O}$ with Rayleigh dehydration is evident by comparison with its closed-system analogue (19). Where $(M_{\text{H}_2\text{O}}/\tau)$ (the oxygen fraction of H_2O) $\ll 1$, the expression for $d\delta^{18}\text{O}_i$ during Rayleigh distillation of H_2O differs from the closed-system equation by $\partial\delta^{18}\text{O}_{\text{sys}}/\partial M_{\text{H}_2\text{O}} d\xi$. It is this additional term which accounts for potentially larger shifts in $\delta^{18}\text{O}_i$ values during Rayleigh dehydration as compared with closed-system reactions. Integration of (29) gives

$$\begin{aligned} \delta^{18}\text{O}_i &= \delta^{18}\text{O}_i^\circ + \sum_k \frac{\nu_k \omega_k \Delta_{ik}^T}{\sum_j \nu_j \omega_j + 1} \ln(\tau + M_{\text{H}_2\text{O}}^\circ + \xi) \\ &+ \sum_k \sum_j \frac{\nu_k \omega_k \omega_j \Delta_{ij}^T}{\sum_s \omega_s (M_s^\circ - \nu_s M_{\text{H}_2\text{O}}^\circ)} \left(M_j^\circ - \frac{\nu_j \tau^\circ}{\sum_l \nu_l \omega_l} \right) \ln \tau \\ &+ \sum_k \sum_j \frac{\nu_k \omega_k \omega_j \Delta_{ij}^T}{\sum_s \omega_s (M_s^\circ - \nu_s M_{\text{H}_2\text{O}}^\circ)} \left(\frac{\nu_j (\tau^\circ + M_{\text{H}_2\text{O}}^\circ)}{\sum_l \nu_l \omega_l + 1} - M_j^\circ \right) \ln(\tau + M_{\text{H}_2\text{O}}^\circ + \xi) \\ &+ \sum_k \frac{\omega_k \Delta_{\text{H}_2\text{O},k}^T}{\sum_s \omega_s (M_s^\circ - \nu_s M_{\text{H}_2\text{O}}^\circ)} \left(M_k^\circ - \frac{\nu_k \tau^\circ}{\sum_l \nu_l \omega_l} \right) \ln \tau \\ &+ \sum_k \frac{\omega_k \Delta_{\text{H}_2\text{O},k}^T}{\sum_s \omega_s (M_s^\circ - \nu_s M_{\text{H}_2\text{O}}^\circ)} \left(\frac{\nu_k (\tau^\circ + M_{\text{H}_2\text{O}}^\circ)}{\sum_l \nu_l \omega_l + 1} - M_k^\circ \right) \ln(\tau + M_{\text{H}_2\text{O}}^\circ + \xi) \end{aligned} \quad (30)$$

Implicit in (30) is the identity $M_{\text{H}_2\text{O}}^\circ + \xi = \omega_{\text{H}_2\text{O}} M_{\text{H}_2\text{O}} = M_{\text{H}_2\text{O}}$. The algebraic complexity of (30) stems from the dependence of τ on ξ according to the relation $\tau = \tau^\circ + \sum_k \nu_k \omega_k \xi$.

The analytical solution for $\delta^{18}\text{O}_i$ as a function of ξ in eq. (30), while cumbersome, illustrates that simultaneous solution of linear differential equations depicting thermochemical equilibrium, mass-balance and isotopic equilibrium can be used to model unambiguously variations in mineral $\delta^{18}\text{O}$ during Rayleigh fractionation processes. In practice, solutions are obtained by numerical integration whereby successive evaluations of the solution vector (e.g. $(\partial\Lambda_j'/\partial M_{\text{H}_2\text{O}})_P$) are used to update continuously the coefficient matrix (e.g. $\partial\theta_i'/\partial\Lambda_j'$).

3.3 Fluid infiltration

In the case of infiltration of fluid, the closed-system equations must be amended to account for variations in both η_i^{sys} and $\delta^{18}\text{O}_{\text{sys}}$, where the system consists of the rock and its pore volume. Consider

the infiltration of aqueous fluid into a metamorphic rock at constant porosity. In this case, the closed-system condition $d\eta_{\text{H}_2\text{O}}^{\text{sys}} = 0$ (constant moles of total system H_2O) is replaced by $dM_{\text{H}_2\text{O}} = 0$ (constant moles of the H_2O phase). The latter is the constraint imposed on the fluid-rock system by fixed porosity (the tacit assumption being that the fluid occupies a dominantly interconnected pore volume). The total $M_{\text{H}_2\text{O}}$ at any instant includes both externally derived H_2O and that produced internally by reaction. Note that we have not thus far altered the total number of independent parameters of the system. Rather, we have simply replaced one extensive constraint with another.

In order to compute the oxygen isotopic effects of fluid infiltration, the closed-system condition $d\delta^{18}\text{O}_{\text{sys}} = 0$ can be replaced by an equation relating $\delta^{18}\text{O}_{\text{sys}}$ to other parameters of the system and the external fluid. The precise form of the equation will depend on the specific circumstance. In all cases, the behavior of the isotopic composition of the external fluid must be specified if an increase in the total number of independent parameters is to be avoided (an analogous statement can be made regarding the mole fraction of fluid components for those cases where multicomponent external fluids are considered).

As an example, we examine the simple case in which the $^{18}\text{O}/^{16}\text{O}$ of the infiltrating H_2O is constant. The equation for $\delta^{18}\text{O}_{\text{sys}}$ in integrated form is then

$$\delta^{18}\text{O}_{\text{sys}} = \sum_s \frac{\omega_s M_s}{\tau} \delta^{18}\text{O}_s + \frac{M_{\text{H}_2\text{O}}^{\text{ext}}}{\tau} \delta^{18}\text{O}_{\text{H}_2\text{O}}^{\text{ext}} + \frac{M_{\text{H}_2\text{O}}^{\text{int}}}{\tau} \delta^{18}\text{O}_{\text{H}_2\text{O}}^{\text{int}} \quad (31)$$

where superscripts “ext” and “int” refer to externally derived H_2O and internally produced H_2O , respectively. The oxygen isotopic composition of the internally produced H_2O in eq. (31), $\delta^{18}\text{O}_{\text{H}_2\text{O}}^{\text{int}}$, is taken to be the value dictated by equilibrium with the solid phases such that only changes in $M_{\text{H}_2\text{O}}^{\text{ext}}$ can affect changes in $\delta^{18}\text{O}_{\text{sys}}$. Incorporation of the identity

$$dM_{\text{H}_2\text{O}}^{\text{ext}} = d\eta_{\text{H}_2\text{O}}^{\text{sys}} \quad (32)$$

followed by differentiation of (31) yields

$$\begin{aligned} d\delta^{18}\text{O}_{\text{sys}} = & \frac{1}{\tau^2} \left(\sum_s \omega_s M_s (\delta^{18}\text{O}_{\text{H}_2\text{O}}^{\text{ext}} - \delta^{18}\text{O}_s) \right) d\eta_{\text{H}_2\text{O}}^{\text{sys}} \\ & + \frac{1}{\tau^2} M_{\text{H}_2\text{O}}^{\text{int}} (\delta^{18}\text{O}_{\text{H}_2\text{O}}^{\text{ext}} - \delta^{18}\text{O}_{\text{H}_2\text{O}}^{\text{int}}) d\eta_{\text{H}_2\text{O}}^{\text{sys}} \end{aligned} \quad (33)$$

Simultaneous solution of eq. (2), (6), (7), (8) and (33) with the conditions $dM_{\text{H}_2\text{O}} = 0$ and $d\eta_{i \neq \text{H}_2\text{O}}^{\text{sys}} = 0$ permits calculation of changes in mineral $\delta^{18}\text{O}$ attending reactions as water with a fixed $^{18}\text{O}/^{16}\text{O}$ flows through the rock at constant porosity.

Returning to the system composed of Ms, Qtz, Kfs, Sil and H_2O at constant pressure, eq. (2), (6), (7), (8) and (33) can be solved to obtain expressions for shifts in $\delta^{18}\text{O}$ with reaction progress, where $d\eta_{\text{H}_2\text{O}}^{\text{sys}} = -d\xi$. The equations to be solved are

$$\frac{\partial \theta_i''}{\partial \Lambda_j''} \left(\frac{\partial \Lambda_j''}{\partial \eta_{\text{H}_2\text{O}}^{\text{sys}}} \right)_p = - \frac{\partial \theta_i''}{\partial \eta_{\text{H}_2\text{O}}^{\text{sys}}} \quad (34)$$

where θ_i'' represents the parameters ($\nu_j \mu_j$, $\eta_{\text{K}_2\text{O}}^{\text{sys}}$, $\eta_{\text{Al}_2\text{O}_3}^{\text{sys}}$, $\eta_{\text{SiO}_2}^{\text{sys}}$, $\eta_{\text{H}_2\text{O}}^{\text{sys}}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, $\delta^{18}\text{O}_{\text{Sil}}$, $\delta^{18}\text{O}_{\text{Kfs}}$, $\delta^{18}\text{O}_{\text{Qtz}}$,

$\delta^{18}\text{O}_{\text{Ms}}$, $\delta^{18}\text{O}_{\text{sys}}$) and Λ_j''' consists of the variable set $(T, M_{\text{Sil}}, M_{\text{Kfs}}, M_{\text{Qtz}}, M_{\text{Ms}}, \delta^{18}\text{O}_{\text{H}_2\text{O}}, \delta^{18}\text{O}_{\text{Sil}}, \delta^{18}\text{O}_{\text{Kfs}}, \delta^{18}\text{O}_{\text{Qtz}}, \delta^{18}\text{O}_{\text{Ms}}, \delta^{18}\text{O}_{\text{sys}})$. Solving for $(\partial\Lambda_j'''/\partial\eta_{\text{H}_2\text{O}}^{\text{sys}})_P$ we have

$$\begin{bmatrix} \left(\frac{\partial T}{\partial\eta_{\text{H}_2\text{O}}^{\text{sys}}}\right)_P \\ \left(\frac{\partial M_{\text{Sil}}}{\partial\eta_{\text{H}_2\text{O}}^{\text{sys}}}\right)_P \\ \left(\frac{\partial M_{\text{Kfs}}}{\partial\eta_{\text{H}_2\text{O}}^{\text{sys}}}\right)_P \\ \left(\frac{\partial M_{\text{Qtz}}}{\partial\eta_{\text{H}_2\text{O}}^{\text{sys}}}\right)_P \\ \left(\frac{\partial M_{\text{Ms}}}{\partial\eta_{\text{H}_2\text{O}}^{\text{sys}}}\right)_P \\ \left(\frac{\partial\delta^{18}\text{O}_{\text{H}_2\text{O}}}{\partial\eta_{\text{H}_2\text{O}}^{\text{sys}}}\right)_P \\ \left(\frac{\partial\delta^{18}\text{O}_{\text{Sil}}}{\partial\eta_{\text{H}_2\text{O}}^{\text{sys}}}\right)_P \\ \left(\frac{\partial\delta^{18}\text{O}_{\text{Kfs}}}{\partial\eta_{\text{H}_2\text{O}}^{\text{sys}}}\right)_P \\ \left(\frac{\partial\delta^{18}\text{O}_{\text{Qtz}}}{\partial\eta_{\text{H}_2\text{O}}^{\text{sys}}}\right)_P \\ \left(\frac{\partial\delta^{18}\text{O}_{\text{Ms}}}{\partial\eta_{\text{H}_2\text{O}}^{\text{sys}}}\right)_P \\ \left(\frac{\partial\delta^{18}\text{O}_{\text{sys}}}{\partial\eta_{\text{H}_2\text{O}}^{\text{sys}}}\right)_P \end{bmatrix} = \begin{bmatrix} 0 \\ -1 \\ -1 \\ 1 \\ 1 \\ \frac{\partial\delta^{18}\text{O}_{\text{sys}}}{\partial\eta_{\text{H}_2\text{O}}^{\text{sys}}} - \nu_s \frac{\partial\delta^{18}\text{O}_{\text{H}_2\text{O}}}{\partial M_s} \\ \frac{\partial\delta^{18}\text{O}_{\text{sys}}}{\partial\eta_{\text{H}_2\text{O}}^{\text{sys}}} - \nu_s \frac{\partial\delta^{18}\text{O}_{\text{Sil}}}{\partial M_s} \\ \frac{\partial\delta^{18}\text{O}_{\text{sys}}}{\partial\eta_{\text{H}_2\text{O}}^{\text{sys}}} - \nu_s \frac{\partial\delta^{18}\text{O}_{\text{Kfs}}}{\partial M_s} \\ \frac{\partial\delta^{18}\text{O}_{\text{sys}}}{\partial\eta_{\text{H}_2\text{O}}^{\text{sys}}} - \nu_s \frac{\partial\delta^{18}\text{O}_{\text{Qtz}}}{\partial M_s} \\ \frac{\partial\delta^{18}\text{O}_{\text{sys}}}{\partial\eta_{\text{H}_2\text{O}}^{\text{sys}}} - \nu_s \frac{\partial\delta^{18}\text{O}_{\text{Ms}}}{\partial M_s} \\ \frac{\partial\delta^{18}\text{O}_{\text{sys}}}{\partial\eta_{\text{H}_2\text{O}}^{\text{sys}}} \end{bmatrix} \quad (35)$$

The solutions illustrate that each aliquot of H_2O added to the system drives reaction (r1) in the negative direction $(-\xi)$, resulting in progressively hydration of the fictive rock. As in the previous examples, (17) applies and the isothermal shifts in $\delta^{18}\text{O}$ are identical for each of the minerals. Substitution of $-\text{d}\xi$ for $\text{d}\eta_{\text{H}_2\text{O}}^{\text{sys}}$ in (34) permits the expression for $\text{d}\delta^{18}\text{O}_i$ to be expanded as

$$\begin{aligned} \text{d}\delta^{18}\text{O}_i = \sum_s \nu_s \omega_s \left[\frac{\Delta_{is}^T}{\tau} - \frac{\sum_j \omega_j \Delta_{ij}^T M_j}{\tau^2} \right] \text{d}\xi \\ - \left[\frac{\sum_k \omega_k M_k (\delta^{18}\text{O}_{\text{H}_2\text{O}}^{\text{ext}} - \delta^{18}\text{O}_k)}{\tau^2} \right] \text{d}\xi \end{aligned} \quad (36)$$

An approximate solution to (36) can be obtained for those instances in which the oxygen isotopic composition of the infiltrating fluid differs significantly from the equilibrium composition such that the

magnitudes of shifts in $\delta^{18}\text{O}_k$ are small compared with $|\delta^{18}\text{O}_{\text{H}_2\text{O}}^{\text{ext}} - \delta^{18}\text{O}_k|$. The latter may then be regarded as constant, yielding upon integration

$$\begin{aligned} \delta^{18}\text{O}_i \approx & \delta^{18}\text{O}_i^\circ + \sum_s \frac{\nu_s \omega_s}{\sum_k \nu_k \omega_k} \left(\Delta_{is}^T \ln \tau + \sum_j \frac{\omega_j \Delta_{ij}^T M_j^\circ}{\tau} \right) \\ & - \sum_s \sum_j \frac{\nu_s \omega_s \nu_j \omega_j \Delta_{ij}^T}{\tau (\sum_k \nu_k \omega_k)} \left(\xi \ln \tau + \frac{\tau^\circ}{\sum_k \nu_k \omega_k} (\ln \tau + 1) \right) \\ & - \sum_k \frac{\omega_k (\delta^{18}\text{O}_{\text{H}_2\text{O}}^{\text{ext}} - \delta^{18}\text{O}_k)}{\tau \sum_j \nu_j \omega_j} \left(\nu_k \xi \ln \tau - M_k^\circ + \frac{\nu_k \tau^\circ}{\sum_j \nu_j \omega_j} (\ln \tau + 1) \right) \end{aligned} \quad (37)$$

Derivation of eq. (37) for this simple example illustrates that variations in mineral $\delta^{18}\text{O}$ values are linked in definite and calculable ways to other chemical parameters (e.g. ξ) during open-system reactions. Integration for more complex cases is normally accomplished numerically and does not require the simplifying assumption of constant $|\delta^{18}\text{O}_{\text{H}_2\text{O}}^{\text{ext}} - \delta^{18}\text{O}_k|$. One concludes that correlations among $\delta^{18}\text{O}$ and macroscopic thermodynamic parameters during progress of open-system reactions can be predicted readily if the behavior of open-system components can be written in linear differential form.

4. Applicability

Exchange of oxygen isotopes among minerals and fluid can occur by resorption and crystallization of minerals (i.e. progress of net-transfer reactions), dissolution and reprecipitation of minerals, and self diffusion of oxygen [17]. The present formalism will be successful in explaining observed variations in mineral $\delta^{18}\text{O}$ if the first process, involving resorption and crystallization of phases during net-transfer reactions, is the predominant mechanism by which at least some metamorphic minerals have acquired their present-day isotopic compositions. The efficacy of these competing processes for redistributing oxygen under metamorphic conditions is examined below in order to provide a context for appraising the usefulness of the calculation method described here. We restrict specific calculations in the following discussion to pelitic bulk compositions at amphibolite facies conditions for ease of expression.

4.1 Progress of metamorphic net-transfer reactions

Shifts in mineral $\delta^{18}\text{O}$ values caused by closed-system reactions (e.g. eq. 20) and devolatilization reactions (e.g. eq. 30) have been investigated previously using largely numerical methods [6,7,18,19]. In general, changes in mineral $\delta^{18}\text{O}$ values produced by closed-system net-transfer reactions are less than approximately 0.5‰ while those associated with devolatilization reactions are less than ca. 1‰. Although of limited use individually, comparisons of such small variations in $\delta^{18}\text{O}$ with mineral elemental concentrations, reaction progress variables (i.e. rock modes), and expected correlations among these variables afforded by the present calculation method is a potentially useful approach for elucidating metamorphic reaction histories.

The range in possible changes in mineral $\delta^{18}\text{O}$ values imparted by concurrent reaction and fluid infiltration during metamorphism (e.g. eq. 37) is commensurate with the possible disparities between $\delta^{18}\text{O}$ values of rocks and fluids. Even for a single instance of disparity between infiltrating fluid and host rock $^{18}\text{O}/^{16}\text{O}$, the potential ensuing changes in $\delta^{18}\text{O}$ are highly variable because of the reciprocal influences of reaction rates and fluid pore velocities.

To appreciate this, consider the equation of mass balance for ^{18}O in a pore of a permeable rock undergoing metamorphism:

$$\frac{\partial C_{^{18}\text{O}}^{\text{pore}}}{\partial t} = -\text{div } J_{^{18}\text{O}}^{\text{inf}} + \frac{\sigma_{\text{pore}}}{v_{\text{pore}}} R_{^{18}\text{O}}^{\text{nt-rxn}} \quad (38)$$

In eq. (38) $C_{18\text{O}}^{\text{pore}}$ is the concentration of ^{18}O in a fluid-filled pore (an adequate approximation for $^{18}\text{O}/^{16}\text{O}$ for the purpose at hand), t is time, $J_{18\text{O}}^{\text{inf}}$ is the advective flux of ^{18}O into the pore attributable to fluid infiltration (moles $^{18}\text{O}/\text{cm}^2/\text{s}$), σ_{pore} is the bounding surface area of the pore, v_{pore} is the volume of the pore, and $R_{18\text{O}}$ is the overall production rate of ^{18}O at pore surfaces (i.e. bounding mineral surfaces) by progress of net-transfer reactions (moles $^{18}\text{O}/\text{cm}^2/\text{s}$). The latter refers to the rate of reaction, irrespective of whether it is controlled by reaction kinetics or the rate of change in ambient conditions which drive the reaction; reactions occurring at or near equilibrium along quasi-statistical paths are not excluded in eq. (38). It is assumed in this formulation that the rates of $^{18}\text{O}^{16}\text{O}_{-1}$ exchange at mineral surfaces are equal to or greater than the rates of net-transfer reactions [e.g. 17].

Two end-member processes affecting changes in mineral $\delta^{18}\text{O}$ are evident from eq. (38). One occurs when the net flux of ^{18}O due to fluid flow through the pores ($\text{div } J_{18\text{O}}^{\text{inf}}$) keeps pace with the rate of ^{18}O production or consumption by reaction at mineral surfaces ($R_{18\text{O}}^{\text{nt-rxn}}$). In these instances the concentration of ^{18}O in the pore fluid is constant so that (38) reduces to

$$\text{div } J_{18\text{O}}^{\text{inf}} = \frac{\sigma_{\text{pore}}}{v_{\text{pore}}} R_{18\text{O}}^{\text{nt-rxn}} \quad (39)$$

and $\delta^{18}\text{O}$ values of newly grown or exposed mineral surfaces will be controlled entirely by the fluid ($\delta^{18}\text{O}_f$) through the relation $\delta^{18}\text{O}_i = \Delta_{if}^T + \delta^{18}\text{O}_f$; i.e. mineral surfaces equilibrate (or strive to equilibrate) with an infinite reservoir of fluid. Although the mathematical treatments which give rise to equations such as (37) are not necessary for simply calculating $\delta^{18}\text{O}$ values in these circumstances, the rigorous treatment is required if the changes in $\delta^{18}\text{O}$ brought about during metamorphism are to be related unambiguously to other variables such as temperature, pressure, mineral elemental concentrations and reaction progress. Fluid-dominated systems for which (39) applies are modeled with the present method by assigning a quantity of fluid large enough to be numerically infinite at each iteration (e.g. $M_{\text{H}_2\text{O}} \gg \sum_s M_s$).

The other end-member process suggested by eq. (38) occurs when the velocity of the fluid cannot keep pace with the rate of reaction such that

$$\text{div } J_{18\text{O}}^{\text{inf}} \ll \frac{\sigma_{\text{pore}}}{v_{\text{pore}}} R_{18\text{O}}^{\text{nt-rxn}} \quad (40)$$

In such cases, new mineral surfaces created during reaction will exhibit $\delta^{18}\text{O}$ values reflecting mass balance among minerals and some finite integrated volume of pore fluid before they are isolated from further exchange of oxygen by new growth. A rigorous mathematical formalism like the one presented here is necessary for predicting changes in $\delta^{18}\text{O}$ in rock-dominated systems open to fluid flow (i.e. where (40) obtains). The form of eq. (37) shows that the extent of reaction and the isotopic composition of the infiltrating fluid can be equally important in determining the $\delta^{18}\text{O}$ values of minerals under these conditions.

From the preceding discourse it should be clear that the relative amounts of fluid and solid used in each step of the model calculations is a *defacto* statement about the relative magnitudes of fluid flux and reaction rate.

4.2 Volume diffusion

In the absence of recrystallization or dissolution, exchange of oxygen isotopes between a mineral interior and its environment will be limited by the rate of oxygen self diffusion in the former. Estimates of oxygen self diffusion coefficients in metamorphic minerals span several orders of magnitude [20,21,22]. Measurements to date indicate that of the porphyroblast-forming minerals common to pelitic bulk compositions, garnet and staurolite are the most resistant to isotopic exchange rate-limited by diffusion while the micas are considerably less refractory.

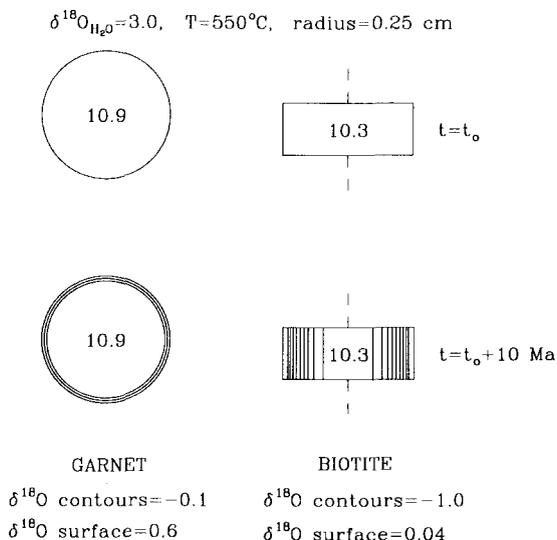


Fig. 1. Effects of self diffusion of oxygen on the isotopic composition of garnet (left) and biotite (right). Surface $\delta^{18}\text{O}$ of both minerals was held constant at values prescribed by equilibrium with an ambient fluid with $\delta^{18}\text{O}$ of 3.0‰ at 550°C. Initial equilibrium $\delta^{18}\text{O}$ for garnet and biotite are 10.9 and 10.3‰, respectively. Oxygen diffusivities for garnet and biotite are 8.49×10^{-26} and 1.04×10^{-7} cm^2/s , respectively, and were calculated with the method of Fortier and Giletti [21]. Garnet was modeled as a sphere ($r = 0.25$ cm) using eq. 6.18 of Crank [38]. Biotite was modeled as an infinite cylinder (axis parallel to c , $r = 0.25$ cm) using eq. 5.22 of Crank [38].

The importance of volume diffusion of oxygen as a means of affecting mineral $\delta^{18}\text{O}$ is quantified by considering the extreme case (see Eiler et al. [23] for a more complete discussion) of a porphyroblast bathed in an aqueous fluid with low $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (3.0‰, cf. equilibrium $\delta^{18}\text{O}$ of 13.3) at 550°C for 10 Ma (time scale suggested by work of Burton and O’Nions [24]) (Fig. 1). Under these conditions, after 10 Ma, spherical garnet with a diameter of 0.5 cm shows virtually no exchange with the ambient fluid; biotite, modeled as a cylinder with a 0.5 cm diameter in which no diffusion occurs parallel to the c axis, exhibits large gradients in $\delta^{18}\text{O}$; and quartz (not shown in Fig. 1) of comparable size is entirely exchanged with the fluid. Results for staurolite are similar to those for garnet. The specifics of these calculations depend on the chosen diffusivities and geometries. The magnitudes of the effects are nevertheless robust and indicate that the $^{18}\text{O}/^{16}\text{O}$ of minerals such as garnet and staurolite are unlikely to be significantly affected by constant-volume exchange with fluid (or solids). These minerals therefore have the potential for preserving the oxygen isotopic record of net-transfer reactions.

4.3 Dissolution–reprecipitation

Dissolution and reprecipitation of minerals in the absence of net-transfer reactions (as commonly defined) can result from gradients in chemical potentials imposed by differences in surface energy among large and small grains which are otherwise in thermochemical equilibrium. This process of grain coarsening, or Ostwald ripening, is potentially important in the evolution of regionally metamorphosed pelites [25,26]. Extensive grain coarsening in the presence of a fluid which has yet to attain isotopic equilibrium with the host rock is a possible mechanism for producing isotopic zoning in large porphyroblasts. Centers of the large grains would retain their original $\delta^{18}\text{O}$ while margins precipitated during coarsening would exhibit $\delta^{18}\text{O}$ approaching equilibrium with the ambient fluid.

Radius–rate relations for Ostwald ripening have been summarized by Joesten [27]. Estimates for the efficacy of porphyroblast coarsening are obtained by assuming that the rate of growth or dissolution is controlled by the flux of the slowest diffusing constituent species through the surrounding matrix

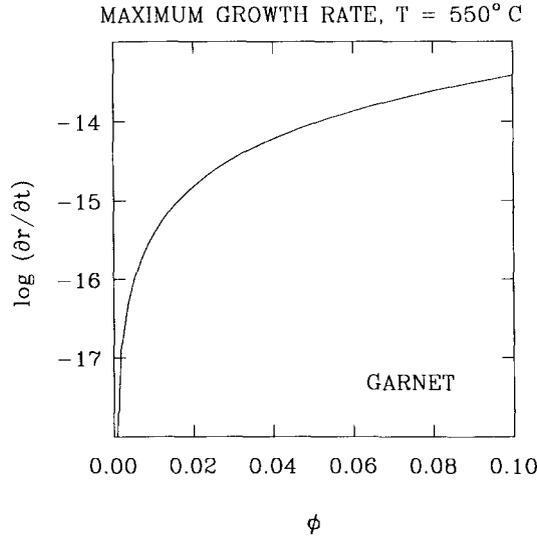


Fig. 2. Plot of the log of maximum rate of radial growth (cm/s) of a spherical garnet by Ostwald ripening as a function of porosity (ϕ) of an enveloping continuum matrix. The garnet exhibiting this maximum rate of growth has a radius r of 0.50 cm in a population of garnets with a mean radius of 0.25 cm. Rate of reaction is assumed to be controlled by diffusion through an interconnected pore fluid at a constant temperature of 550°C (see text). Curve represents solutions to eq. (38) and (39) in the text.

(analyses of other potentially rate-limiting processes such as surface reactions produce similar or slower estimates of growth rate). For this calculation the matrix surrounding the porphyroblast is treated as a continuum in which the transport medium is an interconnected fluid occupying the pore space of the rock. The rate of growth of a spherical grain is then (modified after Joesten [27]):

$$\frac{\partial r}{\partial t} = \frac{2(D_i^T \phi)(x_{i,\text{fluid}}^{\text{eq}} \phi) \gamma \hat{V}_s}{(RT) \hat{r}} \left(\frac{1}{\hat{r}} - \frac{1}{r} \right) \quad (41)$$

where r is the porphyroblast radius, \hat{r} is the average radius for the porphyroblast population, D_i^T is the diffusion coefficient for the slow species i in the fluid at temperature T , ϕ is the porosity, γ denotes the matrix–porphyroblast interfacial energy per unit area, and $x_{i,\text{fluid}}^{\text{eq}}$ represents the equilibrium concentration of diffusing species i in the fluid. Average radius \hat{r} varies with time according to the expression [27]:

$$\hat{r} = \left[\hat{r}^{\circ 3} + \frac{8(D_i^T \phi)(x_{i,\text{fluid}}^{\text{eq}} \phi) \gamma \hat{V}_s}{9(RT)} (t - t^\circ) \right]^{1/3} \quad (42)$$

where \hat{r}° represents the initial average radius at time t° .

As an example, consider a population of garnet porphyroblasts with an average radius of 0.25 cm held at 550°C for 10 Ma in a matrix containing an aqueous interstitial fluid. Solid–solid and solid–fluid interfacial energies differ by no more than a factor of 2 [28], suggesting that γ is less than approximately 2.0×10^{-4} J/cm² [29]. Diffusivities $D_i^{550^\circ\text{C}}$ for major constituent cations of garnet (e.g. Mg⁺⁺, Ca⁺⁺, Si⁺⁺) in the H₂O phase are on the order of 2.0×10^{-4} cm²/s or less [30]. With these upper limits, the maximum growth rate of the garnet porphyroblast, occurring for those grains with a radius of $2\hat{r}$ [27], can be evaluated as a function of matrix porosity ϕ (Fig. 2). Figure 2 illustrates that the importance of Ostwald ripening in redistributing porphyroblast material is critically dependent on ϕ .

Numerical evaluation of eq. (41) and (42) with a value of 5×10^{-3} for ϕ and an average radius of 0.25 cm results in the dissolution–precipitation curves for garnet shown in Fig. 3. Typical growth rates for garnet grains possessing an initial radius significantly greater than the average are on the order of 0.1 cm/10 Ma under these conditions. For a porphyroblast population with a \hat{r} of 0.5 cm, growth rates

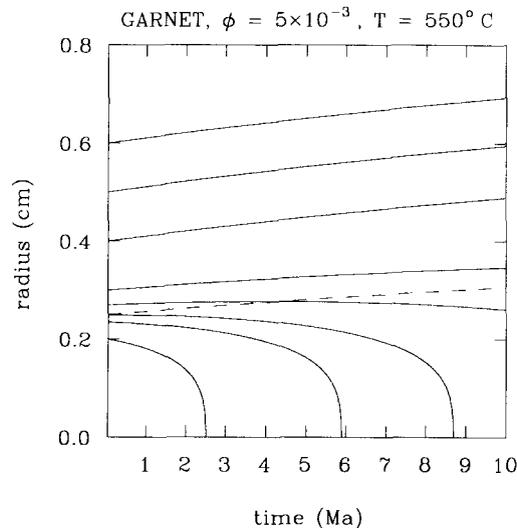


Fig. 3. Radial dissolution-growth curves for garnet porphyroblasts undergoing Ostwald ripening in a continuum matrix with an aqueous fluid-filled porosity of 5×10^{-3} at 550°C . Dashed line shows the evolution of the mean radius \bar{r} of the garnet population. Note that larger grains show a maximum increase in radius of ca. 20% after 10 Ma.

comparable to those in Fig. 3 are obtained with $\phi = 1 \times 10^{-2}$. On the basis of these calculations one can infer that dissolution-precipitation will not be a dominant process for altering $\delta^{18}\text{O}$ values well within interiors of typical coarse-grained porphyroblast minerals *if* porosities are on the order of 5×10^{-3} or less.

Although the calculations presented above are revealing, large uncertainties in the parameters required to evaluate eq. (41) and (42) preclude definitive statements regarding the degree to which mineral $\delta^{18}\text{O}$ are influenced by grain coarsening in the presence of interstitial fluid. Indeed, comparisons of predicted covariations among $\delta^{18}\text{O}$ and mineral cation compositions produced by net-transfer reactions, afforded by the methodology described here, with measured gradients in oxygen isotope ratios and cation concentrations in porphyroblast phases will provide a variety of tests useful for evaluating the relative importance of grain coarsening versus net-transfer reactions in the textural evolution of metamorphosed pelites. Such comparisons should be made using phases such as garnet and staurolite, in which self diffusion of oxygen can be ruled out as a competing process.

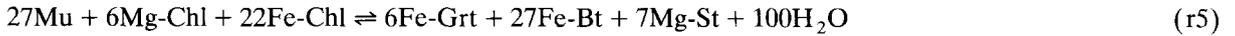
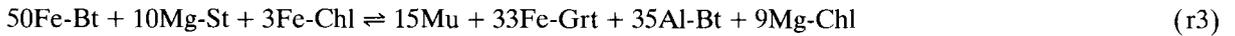
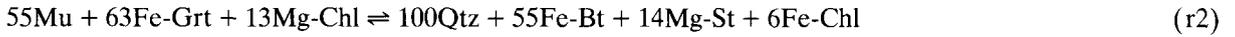
5. Example application

The approach outlined in section 3.3 can be used to elucidate the reaction history which may be recorded by the average intracrystalline gradients in garnet $\delta^{18}\text{O}$ values from a sample of the Gassetts schist of southeastern Vermont. Young and Rumble [5] report average garnet core $\delta^{18}\text{O}$ values of 10.9 and average margin values of 10.0‰. Trial calculations demonstrate that the intracrystalline variations in garnet $\delta^{18}\text{O}$ are too large to be explained by either closed-system reaction or simple dehydration reaction. Marginal values of ca. 10.0‰ extend up to 0.5 cm into the interiors of garnets with radii of approximately 0.8 cm or less [5]. The large radial extent of the isotope heterogeneity suggests, on the basis of calculations presented above (e.g. Fig. 1 and Fig. 3), that grain coarsening and static high-temperature exchange (the latter being ultimately rate limited by volume diffusion) in the presence of low- $\delta^{18}\text{O}$ fluids are not tenable explanations for the observed variations. The data therefore imply the existence of an externally derived (i.e. low- $\delta^{18}\text{O}$) fluid during progress of net-transfer reactions involving garnet.

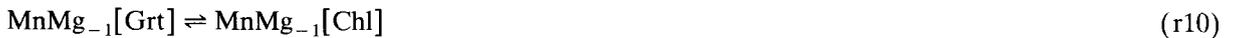
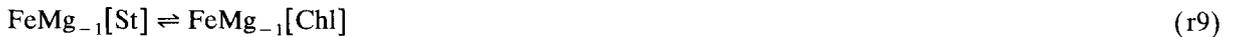
In order to simulate this process using the differential approach, calculations were performed for an initial bulk composition composed of Qtz (12%) + Ms (33%) + Grt (5%) + Bt (12%) + St (21%) + Chl (12%) ± Pl (4.8%) + H₂O (0.2%) (mineral abbreviations after Kretz [31]; abundances in oxygen percent) in the system K₂¹⁶O–Na₂¹⁶O–Ca¹⁶O–Fe¹⁶O–Mg¹⁶O–Mn¹⁶O–Al₂¹⁶O₃–Si¹⁶O₂–H₂¹⁶O–¹⁸O. The relatively small value for $M_{\text{H}_2\text{O}}$ used throughout the calculations means that we are in effect modeling the system as one where the rate of fluid flow is incapable of keeping pace with the rate of reaction (i.e. condition (40)). Implications of this assumption are discussed below.

The initial pressure and temperature were taken as 7000 bar and 540°C, respectively, consistent with estimates for the near-peak metamorphism of the Gassetts schist [32]. The thermochemical data used are from Spear and Cheney [33] and Young [12]. Component activities in solids were defined by mixing-on-sites formulations while the hard-sphere modified Redlich–Kwong equation of state of Kerrick and Jacobs [34] was used for H₂O. Isotope fractionation factors were taken from Richter and Hoernes [35]. Starting $\delta^{18}\text{O}$ values were calculated assuming an initial $\delta^{18}\text{O}_{\text{sys}}$ of 12.1‰. Initial mineral compositions were obtained using a combination of measured garnet, staurolite and mica compositions and published data for similar rocks [5,13,36].

All reactions in the model Gassetts system can be described by combinations of four linearly independent net-transfer reactions:



and six exchange reactions (excluding isotopic exchange):



Al-Bt in (r3) is the aluminous annite component in Bt, KFe₂AlAl₂Si₂O₁₀(OH)₂. Gibbs' phase rule dictates that the system is characterized by 3 intensive degrees of freedom. The total variance, including both intensive and extensive independent parameters, is 12 ($C + 2$, including the amounts of the 9 oxide system components + $\delta^{18}\text{O}_{\text{sys}} + 2$) prior to addition of constraints imposed by degree of mobility of components.

It is assumed that the externally derived H₂O has a constant $\delta^{18}\text{O}$ of 3.0‰, representing, arguably, the lowest $\delta^{18}\text{O}$ typical of metamorphic waters [37]. Equation (33) specifies the behavior of $\delta^{18}\text{O}_{\text{sys}}$ during infiltration of fluid with constant $\delta^{18}\text{O}$, and constitutes an extensive constraint which reduces the total variance of the system from 12 to 11. We also hold that system components other than H₂O and ¹⁸O are invariant, providing 8 additional extensive constraints (i.e. $d\eta_{k \neq \text{H}_2\text{O}}^{\text{sys}} = 0$). Assumption of a constant porosity imparts a 10th restriction, specifically $dM_{\text{H}_2\text{O}} = 0$. There are then 2 remaining linearly independent parameters which must be specified in order to calculate the isotopic and thermochemical evolution of the model system.

Since the goal is to examine the system during infiltration of H₂O, $d\eta_{\text{H}_2\text{O}}^{\text{sys}}$, is taken to be one of the two independent parameters. The value assigned to $d\eta_{\text{H}_2\text{O}}^{\text{sys}}$ is the incremental change in the amount of H₂O used for numerical integration. In this case, it is constrained to be positive in as much as we are concerned with an infiltration process. The magnitude of the increment is somewhat arbitrary, being

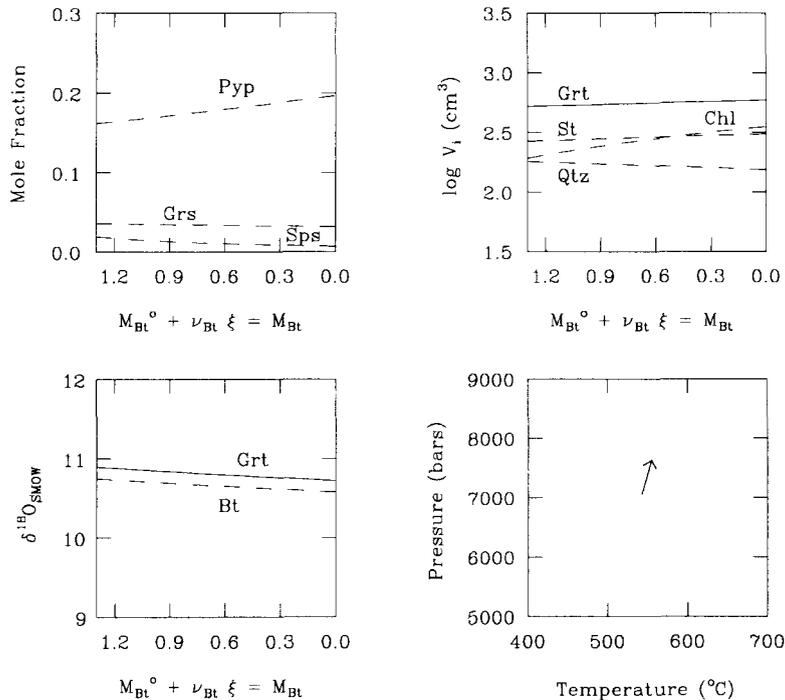


Fig. 4. Changes in mineral $\delta^{18}O$ values, garnet composition (Grs = grossular; Sps = spessartine; Pyp = pyrope), mineral volumetric abundances, and P and T during progress of the garnet-growth reaction path described in the text. Reaction involves fractional growth of both Grt and St in the presence of a low- $\delta^{18}O$ infiltrating aqueous fluid. Note the relatively small shifts in Grt and Bt $\delta^{18}O$.

limited only by the fact that $d\eta_{H_2O}^{sys}$ must be sufficiently small for meaningful numerical integration. A useful magnitude corresponds to the assumed porosity, which in the present calculation is 0.2%. The role of Grt is of particular interest; so it is useful to choose as the final independent parameter dM_{Grt} . The sign and magnitude assigned to dM_{Grt} relative to $d\eta_{H_2O}^{sys}$ dictates the precise reaction path followed by the rock system.

The low diffusivity of oxygen in both garnet and staurolite precludes isotopic equilibration of the interiors of these phases during reaction. The refractory nature of Grt and St was accounted for by addition of equations of the form of (22) (resulting in no change in variance) to simulate their growth or resorption as a Rayleigh fractional process. Invoking fractionation does not significantly alter the results, but is required by preservation of both $\delta^{18}O$ and cation zoning in the garnet.

The system of equations comprising the model Gassetts system was solved by numerical integration using a variety of relative values for dM_{Grt} and $d\eta_{H_2O}^{sys}$. The mechanics of implementing numerical evaluation of the equations has been described elsewhere [13] and is a standard utilization of Jacobian matrices. Figure 4 shows the evolution of the model Gassetts system for dM_{Grt} and $d\eta_{H_2O}^{sys}$ increments of +0.05 moles and +0.2 moles, respectively. Results show that this reaction history, involving garnet growth in the presence of low- $\delta^{18}O$ aqueous fluid, is incapable of explaining the ca. 1‰ zoning in garnet $\delta^{18}O$ at the low relative rate of fluid infiltration implied by the model M_{H_2O} . Higher rates of Grt growth relative to H_2O infiltration yield still smaller shifts in Grt $\delta^{18}O$. Figure 5 shows the evolution of the system for a reaction path corresponding to increments of -0.05 and +0.2 moles for dM_{Grt} and $d\eta_{H_2O}^{sys}$, respectively. This reaction path can explain the recorded shifts in $\delta^{18}O$ in the garnet with low rates of fluid flow. Since the decrease in garnet $\delta^{18}O$ occurs during resorption in Fig. 5, it would only be evident at the absolute rims of fractionating garnets. Formation of low- $\delta^{18}O$ rims of appreciable size, like those found in the Gassetts schist [4,5], would require regrowth of garnet following resorption. The oxygen

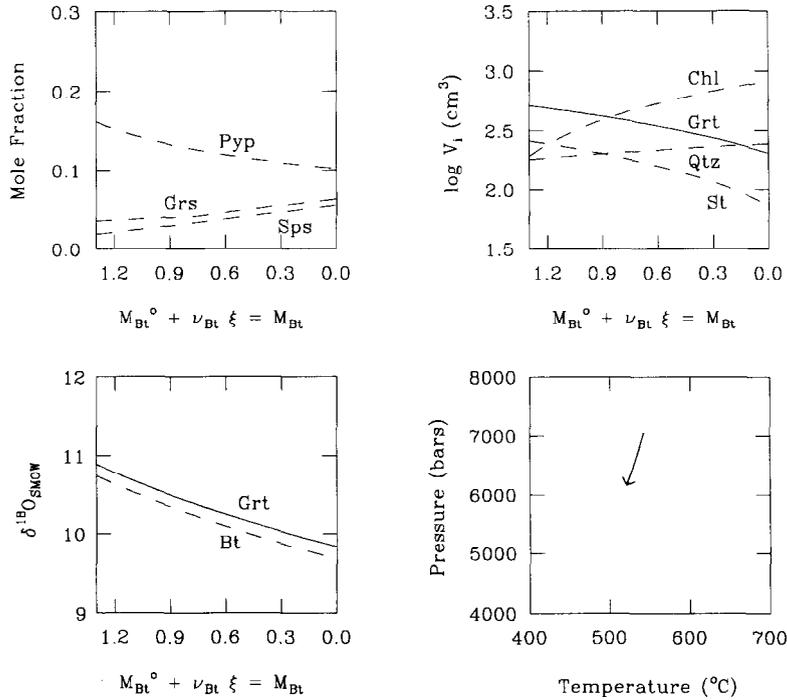


Fig. 5. Changes in mineral $\delta^{18}\text{O}$ values, garnet composition, mineral volumetric abundances, and P and T during progress of the garnet-resorption reaction path described in the text. Reaction involves fractionation of Grt and St in the presence of a low- $\delta^{18}\text{O}$ infiltrating aqueous fluid. Note the significant shift in Grt and Bt $\delta^{18}\text{O}$.

isotope ratios of the newly grown rims would be similar to the absolute rim values in Fig. 5 because, as shown in Fig. 4, even during continued fluid infiltration, fractional garnet growth produces $\delta^{18}\text{O}$ shifts of $\leq 0.3\text{‰}$ provided there is no significant increase in fluid flow rate. This can be visualized if one imagines rerunning the model shown in Fig. 4 starting with the final state of the system in Fig. 5. The contrast between changes in garnet $\delta^{18}\text{O}$ in Figs. 4 and 5 shows that reaction paths can strongly influence the ability of an external fluid to affect changes in mineral $\delta^{18}\text{O}$.

A higher rate of fluid flow relative to garnet growth could be simulated by significantly increasing the value for $M_{\text{H}_2\text{O}}$ used in the calculations. For the same external fluid $\delta^{18}\text{O}$ value, greater amounts of water at each iteration (i.e. greater $M_{\text{H}_2\text{O}}$ for each increment of garnet growth or resorption) would produce larger decreases in garnet $\delta^{18}\text{O}$ than shown in Figs. 4 and 5. As a result, the garnet growth model in Fig. 4 becomes viable for explaining the observed garnet zonation. Alternatively, larger amounts of fluid possessing greater $\delta^{18}\text{O}$ values would give results similar to those in Figs. 4 and 5. In short, the oxygen isotopic composition of the infiltrated fluid cannot be determined without prior knowledge of the rate of fluid flow relative to the rate of net-transfer reaction progress and *vice versa*. The reaction path which attended fluid infiltration can still be constrained, however, because simultaneous solution of isotope ratio and thermodynamic equations affords additional information bearing on whether or not the garnet $\delta^{18}\text{O}$ zonation is the product of growth or resorption.

The model calculations predict the covariations among garnet cation concentrations and $\delta^{18}\text{O}$ values which should be recorded in the garnets for the computed reaction paths. The correlation between X_{Sps} and $\delta^{18}\text{O}$ is positive for the garnet-growth path (Fig. 4) and negative for the garnet-resorption path (Fig. 5). Negative correlations between these parameters are exhibited by the Gassetts garnets as abrupt increases in Mn concentrations coincident with the shift from a core $\delta^{18}\text{O}$ value of 10.9 to a margin value

of 10.0‰ [5], suggesting that the garnet-resorption scenario is the best explanation for the available data.

In this example, the differential equation approach to modeling isotopic shifts attending net-transfer reactions reveals that $\delta^{18}\text{O}$ and cation zonations in the garnets of interest can be explained by two stages of garnet growth separated by an episode of garnet resorption during infiltration of a low- $\delta^{18}\text{O}$ aqueous fluid. The precise fluid $\delta^{18}\text{O}$ involved in the garnet-resorption reaction is a function of the inferred rate of fluid flow relative to the reaction rate (eq. 38).

6. Conclusions

The differential equation approach to modeling variations in mineral $\delta^{18}\text{O}$ in metamorphic rocks has much to recommend it over other methods. The principal advantage is that the inherent dependencies among $\delta^{18}\text{O}$ and other thermochemical parameters are accounted for rigorously, eliminating the need for *ad-hoc* relations among parameters (cf. the relation between T and ξ required in [6,7]). The equations can be modified to accommodate a variety of metamorphic conditions, including fractional loss of fluid, fractional growth of mineral phases, and fluid infiltration. Comparisons of predicted covariations among $\delta^{18}\text{O}$ values, cation concentrations, and mineral abundances to patterns preserved in natural rocks provide useful tools for deciphering metamorphic net-transfer reaction histories. In addition, such comparisons provide a means for determining the relative importance of competing processes, such as Ostwald ripening, during the textural evolution of metamorphic rocks. Garnet and staurolite are particularly well suited for these purposes because of their resistance to post-growth oxygen exchange. The method of calculation presented here constitutes the necessary framework for evaluating small-scale variations in $\delta^{18}\text{O}$ in the context of parageneses in metamorphic rocks.

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