

Appendix A

Open System Diffusion Modelling of Coronas.

Modelling methodology is derived fully in a series of papers: Fisher, (1973, 1975, 1977); Joesten, (1977); Carlson & Johnson, (1991); Ashworth and Sheplev, (1997). A brief summary of the method outlined by Ashworth and Sheplev (1997) is presented below. All symbols used in the equations below are listed in Table 1.

There are 3 basic equations (Fisher, 1970; Joesten, 1977), which respectively relate:

- Component fluxes J_i to chemical potential gradients ($d\mu_i / dx$) such that for each component $i=1$ to S

$$J_i = -\sum_{j=1}^S L_{ij} \frac{d\mu_j}{dx} \quad \mathbf{A1}$$

L_{ij} are phenomenological coefficients for diffusion in an multi-component system (Joesten, 1977). Straight coefficients ($i \neq j$) relate diffusion of component i to the chemical potential gradient of i and the cross coefficients ($i = j$) relate diffusion of component i to the chemical potential gradient of j . Joesten (1977) and Fisher (1970) assume that the contribution of terms involving cross-coefficients is negligible.

- Chemical potential gradients to each other in the presence of a mineral m , in which the molar content of component i is n_{im} , such that in a layer containing m ,

$$\sum_{i=1}^S n_{im} \frac{d\mu_i}{dx} \quad \mathbf{A2}$$

Table A.1: Symbols used in derivation of open system diffusion models (modified after Ashworth and Sheplev, 1997)

A_{kl}	Coefficient defined in equation 9 for phases k and l
a	Area of layers, in the plane perpendicular to fluxes (m^2)
G_k	Molar free energy of phase k ($J mol^{-1}$)
G_k^f	Molar free energy of phase k dissolved in fluid or intergranular medium ($J mol^{-1}$)
$(-\Delta G)$	Affinity of overall reaction ($J mol^{-1}$)
$(-\Delta G)^*$	Model affinity of overall reaction ($m^3 mol^{-1}$)
h^r	Thickness of layer r (m)
h^{r*}	Model layer thickness ($m^3 mol^{-1}$)
J_i^r	Flux of component i in layer r ($mol m^{-2} s^{-1}$)
J_i^{r*}	Model flux of component i in layer r (mol/mol reaction progress).
L_{ij}	Onsager diffusion coefficients ($mol^2 J^{-1} m^{-1} s^{-1}$)
n_{ik}	Number of moles of component i in 1 mole of phase k .
q^k	Number of the boundary where phase k first appears.
R	Gas constant ($8.3145 J K^{-1} mol^{-1}$)
t	Time (s)
T	Temperature (K)
x	Distance parallel to fluxes (m)
μ_i^r	Chemical potential of component i at boundary r ($J mol^{-1} m^{-1}$)
$(d\mu_i / dx)^r$	Chemical potential gradient of component i at boundary r ($J mol^{-1} m^{-1}$)
$(d\mu_i / dx)^{r*}$	Model chemical potential of component i at boundary r (mol/mol reaction progress).
v_k	Stoichiometric coefficient of phase k in overall reaction.
$(v_k')^q$	v_k minus amount attributed to recurrence of k to right of layer q .
v_k^r	Stoichiometric coefficient of phase k in reaction at boundary r .
\mathcal{E}	Overall reaction progress (mol)
\mathcal{E}'	Overall reaction progress per unit area ($mol m^{-2}$)
Φ	Number of phases
Φ^q	Number of phases in layer q .

- Flux change between layers $r-1$ and r to the stoichiometric coefficients v_k^r of minerals k in the reaction at boundary r , such that for mass conservation and local mass balance at boundary r

$$J_i^r = J_i^{r-1} + \frac{d\varepsilon'}{dt} \sum_{k=1}^{\Phi} n_{ik} v_k^r \quad \mathbf{A3}$$

In equation 3, v_k^r is positive if k is consumed at boundary r .

Ashworth and Sheplev (1997) use the modified form of the reaction progress variable (ξ) appropriate to layer growth,

$$\varepsilon' = \varepsilon/a$$

where a is the area of the layer structure

The factor $\frac{d\varepsilon'}{dt}$ in eqn A3 converts $n_{ik} v_k^r$ (moles of component per mole of reaction progress) to J_i^r in its true units (mol component $\text{m}^{-2}\text{s}^{-1}$).

Intrinsic to the model is mass balance. An overall reaction is reconstructed using the measured proportion of phases to derive an open-system reaction, with boundary fluxes representing metasomatic interaction with the surrounding rock. The overall reaction may be summarised by a mass balance for each component i .

$$\sum_{k=1}^{\Phi} v_k n_{ik} = 0 \quad \mathbf{A4 (eqn 5.1)}$$

In a closed-system, the summation is over all minerals k . In an open system, the metasomatic fluxes at the end boundaries are treated as imaginary phases Met_1 and Met_2 respectively with unit stoichiometric coefficients $v_{\text{met}_1} = v_{\text{met}_2} = 1$ (always positive if entering system – always negative if leaving system).

For a given overall reaction, one large set of simultaneous equations can be written constraining a postulated layer sequence. Reaction coefficients are calculated at each layer boundary systematically from left to right. Iteratively varying the postulated

L-ratios in equation A1 will lead to varying distributions of minerals among layers. An acceptable model must approximately match the observed distribution.

Determination of reaction coefficients v_k^q at boundaries q for a postulated layer sequence involves simultaneous solution of equations A1-3. The summation of equation A3 over boundaries 1 to q gives the flux of component i in layer q . This includes the ‘artificial’ phase Met_1 , thereby accommodating the metasomatic fluxes at boundary 1.

$$J_i^q = \frac{d\varepsilon'}{dt} \sum_{k=1}^{\Phi} n_{ik} \sum_{r=1}^q v_k^r \quad \text{A5}$$

With $L_{ij} = 0$ for $i \neq j$, Eqn A1 can be rearranged as

$$\left(\frac{d\mu_i}{dx} \right)^q = \frac{-J_i^q}{L_{ii}} \quad \text{A6 (eqn 5.3)}$$

The unknown fluxes J_i^q and chemical potential gradients $(d\mu_i/dx)^q$ are to be eliminated between equations A2, A5 and A6. Substituting $(d\mu_i/dx)^q$ in equation A2 gives

$$\sum_{i=1}^S n_{im} \frac{J_i^q}{L_{ii}} = 0 \quad \text{A7}$$

...for $m = 1, \dots, \Phi^q$, where Φ^q is the number of minerals in layer q .

Then substituting for J_i^q from eqn A5 in eqn A7 gives...

$$\sum_{i=1}^S \frac{n_{im}}{L_{ii}} \sum_{k=1}^{\Phi} n_{ik} \sum_{r=1}^q v_k^r = 0 \quad \text{A8}$$

...for $m = 1, \dots, \Phi^q$, where Φ^q is the number of minerals in layer q .

The equations are solved for cumulative reaction coefficients, up to boundary q , of those minerals present in layer q . The phase compositions (n_{ik} for all i, k) and chosen values of L_{ii}/L_{SiSi} are required inputs.

To facilitate computation, Ashworth and Birdi (1990) defined a quantity A_{kl} which is calculated for each pair of minerals k and l .

$$A_{kl} = \sum_{i=1}^S \frac{L_{SiSi}}{L_{ii}} n_{ik} n_{il} \quad \mathbf{A9}$$

Equation A8 is simplified for each mineral m in layer q :

$$\sum_{k=1}^{\Phi} A_{mk} \sum_{r=1}^q v_k^r = 0$$

Ashworth and Birdi (1990) then divided the summation over phases $k = 1$ to Φ into two steps: (1) Summation for Φ^q minerals present in layer q (whose coefficients are unknowns); (2) Summation for the remaining phases between boundaries 1 and q (Φ^{left}).

Mass balance requires:

$$\sum_{k=1}^{\Phi^q} A_{mk} \sum_{r=1}^q v_k^r = - \sum_{k=\Phi^q+1}^{\Phi^q+\Phi^{left}} A_{mk} (v_k^r)^q \quad \mathbf{A10}$$

where $(v_k^r)^q$ is v_k if the Φ^{left} minerals are present only to the left of layer q .

If a layer sequence is computationally acceptable, then the molar amount of each mineral in each layer is obtained and layer thicknesses are found using the molar volumes of the minerals. The thickness computed above is not the absolute thickness – but the thickness per unit reaction progress.

$$h^{r*} = h^r / \varepsilon' \quad \mathbf{A11}$$

...and

$$J_i^{r*} = \frac{J_i^r}{d\varepsilon'/dt}$$

A model is considered successful if ratios among the thicknesses h^{r*} and the proportions of minerals in layers, match the observed corona layers. However, before finally accepting a model, a thermodynamic stability criterion derived by Ashworth and Sheplev (1997) must be satisfied. Furthermore, the most stable solution may be isolated if several non-unique solutions are predicted by the model.

The stability criterion is based on the premise that in a layer where mineral k is absent, the diffusion medium should not be super-saturated with respect to k . If mineral k coexists with an intergranular medium at local equilibrium, the chemical potential of each component in the mineral is equal to the chemical potential of the corresponding component in the intergranular medium (Ashworth and Sheplev, 1997). The Gibbs free energy of the mineral, G_k , can be computed from the chemical potentials and the mineral compositions via the following equation:

$$G_k = \sum_{i=1}^S n_{ik} \mu_i$$

A12 (eqn 5.4)

Similarly, Ashworth and Sheplev (1997) defined a quantity measuring the chemical potential of component k in the intergranular medium, i.e. G_k^f

$$G_k^f = \sum_{i=1}^S n_{ik} \mu_i$$

A13 (eqn 5.6)

At local equilibrium between the mineral and the intergranular medium, $G_k^f = G_k$. If $G_k^f > G_k$ the diffusion medium is supersaturated with respect to k . Thus, wherever k is absent: $G_k^f < G_k$. Ashworth and Sheplev (1997) related the variation in G_k^f across a layered structure to layer thickness and chemical potential gradients. The chemical potential gradient μ_i^q at boundary q is:

$$\mu_i^q = \mu_i^1 + \sum_{r=1}^{q-1} h^{r*} \left(\frac{d\mu_i}{dx} \right)^{r*}$$

and $(G_k^f)^q$ at this boundary is:

A14

$$(G_k^f)^q = \sum_{i=1}^s n_{ik} \left[\mu_i^1 + \sum_{r=1}^{q-1} h^{r*} \left(\frac{d\mu_i}{dx} \right)^{r*} \right]$$

A15

A successful corona model yields h^{r*} and $\left(\frac{d\mu_i}{dx}\right)^{r*}$ which are proportional to h^r and $\left(\frac{d\mu_i}{dx}\right)^r$. Ashworth and Sheplev (1997) described the differences across layers in a quantity $(G_k^f)^*$:

$$\left[(G_k^f)^q - (G_k^f)^1 \right]^* = \sum_{i=1}^s n_{ik} \sum_{r=1}^{q-1} h^{r*} \left(\frac{d\mu_i}{dx} \right)^{r*}$$

A16 (eqn 5.7)

$\left[(G_k^f)^q - (G_k^f)^1 \right]^*$ has a constant value in all layers where mineral k is present. Stability criterion is satisfied if equation A16 gives a lower value of $\left[(G_k^f)^q - (G_k^f)^1 \right]^*$ at all boundaries where mineral k is absent than this constant value $\left[G_k - (G_k^f)^1 \right]^*$. Subtracting this constant value gives $\left[(G_k^f)^q - G_k \right]^*$ - the layer sequence is stable if this is everywhere ≤ 0 .

Prigogine and Defay, (1954) defined the affinity of a reaction as follows:

$$(-\Delta G) = \sum_{k=1}^{\phi} \nu_k G_k$$

A17

Ashworth and Sheplev (1997) applied this equation to layered coronas. At every point in the corona where local equilibrium is attained, the reaction affinity equals zero. However, the presence of chemical potential gradients between layers in a corona drives diffusion and generates a reaction affinity.

A phase k present at boundary q has molar free energy given by the following equation:

$$G_k = \sum_{i=1}^s n_{ik} \mu_i$$

A12 (eqn 5.4)

Ashworth and Sheplev (1997) then merged the two equations above with equation A15 to yield:

$$(-\Delta G) = \sum_{k=1}^{\phi} v_k \sum_{i=1}^s n_{ik} \left[\mu_i^1 + \sum_{r=1}^{q^k-1} h^r \left(\frac{d\mu_i}{dx} \right)^r \right]$$

A18

The boundary at which phase k first appears is q^k . The summation inside the brackets is different for different minerals, but μ_i^1 is a constant and drops out, by the equation below.

$$\sum_{k=1}^{\phi} v_k n_{ik} = 0$$

thus

A19

$$\mu_i^1 \sum_{k=1}^{\phi} v_k n_{ik} = \mu_i^1 \cdot 0 = 0$$

This simplification allowed Ashworth and Sheplev (1997) to obtain the following critical equation relating chemical potential differences across layers to reaction affinity:

$$(-\Delta G) = \sum_{k=1}^{\phi} v_k \sum_{i=1}^s n_{ik} \sum_{r=1}^{q^k-1} h^r \left(\frac{d\mu_i}{dx} \right)^r$$

A20

The corresponding model affinity (Ashworth and Sheplev, 1997) is calculated as follows.

$$(-\Delta G) = \sum_{k=1}^{\phi} v_k \sum_{i=1}^s n_{ik} \sum_{r=1}^{q^k-1} h^{r*} \left(\frac{d\mu_i}{dx} \right)^{r*}$$

A21 (eqn 5.11)

Matrix notation

Solution of the systems of linear equations described above is best written in matrix notation for simplicity (Ashworth and Sheplev, 1997). Matrix notations (and MATLAB equivalents) are included in Table 2.

The quantity A_{kl} of equation A9 is an element of the $\Phi \times \Phi$ matrix:

$$\mathbf{A} = \mathbf{N}^T (\mathbf{L}^*)^{-1} \mathbf{N}$$

The elements of the \mathbf{L}^* matrix are the input L-ratios L_{ij}/L_{SiSi} . \mathbf{N} gives the measured phase compositions.

If \mathbf{N}^q contains the compositions of phases in layer q , then define \mathbf{A}^q as follows:

$$\mathbf{A}^q = (\mathbf{N}^q)^T (\mathbf{L}^*)^{-1} \mathbf{N}^q$$

Similarly, define \mathbf{N}_{left}^q by substituting zero vectors for all phases present in layer q or to the right layer q , such that:

$$\mathbf{A}_{left}^q = (\mathbf{N}^q)^T (\mathbf{L}^*)^{-1} \mathbf{N}_{left}^q$$

Equation A10 in matrix notation becomes:

$$\mathbf{A}^q \sum_{r=1}^q (\bar{v}^{q+})^r = -\mathbf{A}_{left}^q (\bar{v}')^q$$

Column vector $(\bar{v}^{q+})^r$ contains reaction coefficients, at boundary r , of the phases present in layer q . $(\bar{v}')^q$ is a column vector containing the overall reaction coefficients (which may be modified if the mineral occurs to the right of layer q). Now the equation is solved for reaction coefficients at boundary r .

$$\sum_{r=1}^q (\bar{v}^{q+})^r = -(\mathbf{A}^q)^{-1} \mathbf{A}_{left}^q (\bar{v}')^q$$

Ashworth and Sheplev (1997) define a transitional matrix which assists in calculated model component fluxes and chemical potential gradients across each layer.

$$\mathbf{B}^q = (\mathbf{L}^*)^{-1} \left[\mathbf{N}^q (\mathbf{A}^q)^{-1} \mathbf{A}_{left}^q - \mathbf{N}_{left}^q \right]$$

Fluxes are computed by summing amounts of components evolved in reactions up to boundary q as follows:

$$\bar{J}^{q*} = \mathbf{N}^q \sum_{r=1}^q (\bar{v}^{q+})^r + \mathbf{N}_{left}^q (\bar{v}')^q = -\mathbf{L}^* \mathbf{B}^q (\bar{v}')^q$$

Chemical potential gradients are readily computed from model fluxes though the following matrix equation:

$$(d\bar{\mu}/dx)^{q*} = -(\mathbf{L}^*)^{-1} \bar{J}^{q*} = \mathbf{B}^q (\bar{v}')^q$$

Matrices required for evaluation of the thermodynamic stability criterion are as follows:

$$\left[(\bar{G}_k^f)^q - (\bar{G}_k^f)^1 \right]^* = (\bar{N}_k)^T \sum_{r=1}^{q-1} h^{r*} \mathbf{B}^r (\bar{v}')^r$$

\bar{N}_k is the vector of n_{ik} for phase k . $\left[(\bar{G}_k^f)^q - (\bar{G}_k^f)^1 \right]^*$ has a constant value in all layers where mineral k is present. Stability criterion is satisfied if values of $\left[(\bar{G}_k^f)^q - (\bar{G}_k^f)^1 \right]^*$ at all boundaries where k is absent are lower than this constant value $\left[\bar{G}_k - (\bar{G}_k^f)^1 \right]^*$. Subtracting this constant value gives $\left[(\bar{G}_k^f)^q - \bar{G}_k \right]^*$ - the layer sequence is stable if this is everywhere ≤ 0 .

In this study, reaction affinity was calculated through an algorithm in an EXCEL spreadsheet. However, it is possible to complete the computation of reaction affinity using matrix algebra as follows. Ashworth and Sheplev (1997) calculate model affinity $(-\Delta G)^*$ by summing the difference in each G_k^* between a reference boundary and a boundary where k is present. These authors use boundary 1 as a reference and evaluate reaction affinity at the right-hand boundary, such that $q=K$. Computation is simple since matrix \mathbf{N}_{left}^q is already defined for minerals present to the left of each layer q . A transitional matrix \bar{b} is defined as follows:

$$\bar{b} = -\sum_{q=1}^{K-1} h^{q*} (\mathbf{N}_{left}^q)^T \mathbf{B}^q (\bar{v}')^q$$

Vector \bar{b} is related to $(-\Delta G)^*$:

$$\bar{b} = \left[\bar{G} - (\bar{G}^f)^K \right]^*$$

$$(-\Delta G)^* = \bar{v}^T \bar{b}$$

Table A.2: Matrices used in derivation of open system diffusion models

Matrix Notation	MATLAB			
Ashworth & Sheplev (1997)	Notation (This study)	Dimensions	Element	Description
A	A	$\Phi \times \Phi$	A_{kl}	A_{kl} as defined in equation 9.
A^q	Aq(1,2,3...)	$\Phi^q \times \Phi^q$	A_{kl}	A_{kl} for minerals in layer q .
A^q_{left}	AqL(1,2,3...)	$\Phi^q \times \Phi$	A_{kl}	A_{kl} for minerals in layer q , zero unless l is absent from layer q but present further left
B^q	Bq(1,2,3...)	$S \times \Phi$		Defined in layer q
\bar{b}		$\Phi \times 1$		Defined in layer q
$(\bar{G}_k^f)^{q*}$	-	$\Phi \times 1$	$(G_k^f)^q$	Model molar free energies of phase dissolved in fluid or intergranular medium. Evaluates saturation state of intergranular medium with respect to mineral k . [mol ² component/(mol mineral)*(mol reaction progress)]
\bar{G}_k^* or \bar{G}^*	-	$\Phi \times 1$	G_k	Model molar free energies of phases [mol ² component/(mol mineral)*(mol reaction progress)]
-	Gfkgrd	$\Phi \times r$	G_k	Model free energy gradients for mineral k in each layer $[dG_k^f/dx]^{r*}$ [mol ² component/(mol mineral)*(mol reaction progress)]
-	Gfkdiff(1,2,3...)	$\Phi \times 1$	G_k	Model free energy differences across each layer r , $[(G_k^f)^{r+1} - (G_k^f)^r]^*$ [10 ⁻⁴ m ³ mol ² component/(mol mineral)*(mol ² reaction progress)]
-	Gfkdiffvs1	$\Phi \times r$	G_k	Model free energy differences at boundary q from those at boundary 1, $[(G_k^f)^q - (G_k^f)^1]^*$ [10 ⁻⁴ m ³ mol ² component/(mol mineral)*(mol ² reaction progress)]

Table A.2: Matrices used in derivation of open system diffusion models

Matrix Notation	MATLAB			
Ashworth & Sheplev (1997)	Notation (This study)	Dimensions	Element	Description
\bar{J}^q	-	$S \times 1$	J_i^r	Fluxes of components in layer q (mol/mol reaction progress).
\bar{J}^{q*}	Jq(1,2,3...)	$S \times 1$	J_i^{r*}	Model fluxes of components in layer q (mol/mol reaction progress).
\mathbf{L}^*	L	$S \times S$	L_{ij} / L_{SiSi}	Ratios of Onsager diffusion coefficients
\bar{N}_k	-	$S \times 1$	n_{ik}	Composition of phase k .
\mathbf{N}	N	$S \times \Phi$	n_{ik}	Compositions of all phases k .
\mathbf{N}^q	Nq(1,2,3...)	$S \times \Phi^q$	n_{ik}	Composition of phases in layer q .
\mathbf{N}_{left}^q	NqL(1,2,3...)	$S \times \Phi$	n_{ik}	Compositions of phases in layer q , zero unless k is absent from layer q but present further left.
$(d\bar{\mu}/dx)^{q*}$	Cp(1,2,3...)	$S \times 1$	$(d\mu_i / dx)^{r*}$	Model chemical potential gradients for components in layer q .
\bar{v}	X	$\Phi \times 1$	v_k	Overall reaction coefficients of all phases
$(\bar{v}')^q$	X	$\Phi \times 1$	$(v'_k)^q$	Modified \bar{v} if a mineral occurs to the right of layer q .
\bar{v}^r	Vq(1,2,3...)	$\Phi \times 1$	v_k^r	Reaction coefficients at boundary r .
$(\bar{v}^{q+})^r$	Vq(1,2,3...)	$\Phi^q \times 1$	v_k^r	Reaction coefficients for minerals present in layer q .

MATLAB SCRIPT

Open system diffusion modelling of coronas in this study was performed in MATLAB. The MATLAB script for modelling of a three layer coronas is included below:

```
NT=N'
```

```
L
```

```
A=NT*L*N
```

```
Nq1
```

```
Nq1T=Nq1'
```

```
Aq1=Nq1T*L*Nq1
```

```
Nq1L
```

```
Aq1L=Nq1T*L*Nq1L
```

```
Vq1 = -inv(Aq1)*Aq1L*X
```

```
Bq1= L*(Nq1*inv(Aq1)*Aq1L-Nq1L)
```

```
Jq1=-1*inv(L)*Bq1*X
```

```
Cp1=Bq1*X
```

```
Nq2
```

```
Nq2T=Nq2'
```

```
Aq2=Nq2T*L*Nq2
```

```
Nq2L
```

```
Aq2L=Nq2T*L*Nq2L
```

```
Vq2 = -inv(Aq2)*Aq2L*X
```

```
Bq2= L*(Nq2*inv(Aq2)*Aq2L-Nq2L)
```

```
Jq2=-1*inv(L)*Bq2*X
```

```
Cp2=Bq2*X
```

```
Nq3
```

```
Nq3T=Nq3'
```

Aq3=Nq3T*L*Nq3

Aq3L=Nq3T*L*Nq3L

Nq3L

Aq3L=Nq3T*L*Nq3L

Vq3 = -inv(Aq3)*Aq3L*X

Bq3= L*(Nq3*inv(Aq3)*Aq3L-Nq3L)

Jq3=-1*inv(L)*Bq3*X

Cp3=Bq3*X

% compile Cpt

Cpt=[Cp1(:,1), Cp2(:,1), Cp3(:,1)]

Gfkgrd=NT*Cpt

Gfkdiff1 = h1 *Gfkgrd

Gfkdiff2 =h2*Gfkgrd

Gfkdiff3=h3*Gfkgrd

% Compile Jqt

Jqt=[Jq1(:,1), Jq2(:,1), Jq3(:,1)]

% compile Gfkdiff

Gfkdiff=[Gfkdiff1(:,1), Gfkdiff2(:,2), Gfkdiff3(:,3)]

Gfkdiffvs1 = [Gfkdiff(1,1) Gfkdiff(1,1)+Gfkdiff(1,2) Gfkdiff(1,1)+Gfkdiff(1,2)+Gfkdiff(1,3); Gfkdiff(2,1)

Gfkdiff(2,1)+Gfkdiff(2,2) Gfkdiff(2,1)+Gfkdiff(2,2)+Gfkdiff(2,3); Gfkdiff(3,1) Gfkdiff(3,1)+Gfkdiff(3,2)

Gfkdiff(3,1)+Gfkdiff(3,2)+Gfkdiff(3,3); Gfkdiff(4,1) Gfkdiff(4,1)+Gfkdiff(4,2) Gfkdiff(4,1)+Gfkdiff(4,2)+Gfkdiff(4,3);

Gfkdiff(5,1) Gfkdiff(5,1)+Gfkdiff(5,2) Gfkdiff(5,1)+Gfkdiff(5,2)+Gfkdiff(5,3); Gfkdiff(6,1) Gfkdiff(6,1)+Gfkdiff(6,2)

Gfkdiff(6,1)+Gfkdiff(6,2)+Gfkdiff(6,3); Gfkdiff(7,1) Gfkdiff(7,1)+Gfkdiff(7,2) Gfkdiff(7,1)+Gfkdiff(7,2)+Gfkdiff(7,3);

Gfkdiff(8,1) Gfkdiff(8,1)+Gfkdiff(8,2) Gfkdiff(8,1)+Gfkdiff(8,2)+Gfkdiff(8,3)]

Non-equilibrium thermobarometry

The application of thermobarometric techniques requires that all phases considered are in equilibrium. This assumption is not valid for coronas where chemical potential gradients exist across the layered reaction band. In conventional thermobarometry, all independent endmember reactions defining the system are assumed to have zero affinity ($-\Delta G = 0$). In the case of coronas in disequilibrium, endmember reactions have a finite affinity, which are readily calculated from open system diffusion modelling (e.g., Attoh, 1998; Markl et al., 1998). The model affinities (and chemical potential gradients from which they are determined) are dimensionless because of the use of diffusion coefficient ratios. However, if a model successfully reproduces corona growth, then ratios amongst the *model* chemical potential gradients and affinities must be the same as the *real* chemical potential gradient and affinity ratios. The model affinity ratios can then be compared with real affinity ratios for endmember reactions in the system computed independently from an internally consistent thermodynamic database (Holland and Powell, 1998; Nov 2003 upgrade) at a range of P and T . A fit between the model ratios and real computed ratios must be found at the P and T of corona formation. The assumption of a constant P and T is not valid for the entire corona-forming reaction, but Ashworth et al. (2001) argue that it is a reasonable assumption for most coronas. The validity of the assumption must be established when reviewing non-equilibrium thermobarometric P - T estimates.

The modelling procedure is as follows (after Ashworth et al., 2001):

The model chemical potential gradient for end-member j across growing layer r is:

$$(d\mu_j / dx)^{r*} = \sum_i n_{ij} (d\mu_i / dx)^{r*}$$

where n_{ij} is the number of moles of component i in one mole of j . The composition of a mineral containing j at a particular location in the corona provides a reference location for μ_j^* . The difference between μ_j^* and another place in the corona where the same mineral, but with different composition, is measured, gives rise to a chemical potential gradient. If the reference location is at a boundary between

layers, then the difference at some other boundary is the sum of the differences across layers. If the reference boundary for j is q_j , then at boundary q ,

$$\left(\mu_j^{q_j} - \mu_j^q\right)^* = -\sum_{r=q_j}^{q-1} h^{r*} (d\mu_j / dx)^{r*} \text{ if } q_j < q \quad \mathbf{A22a (eqn 5.9a)}$$

$$\left(\mu_j^{q_j} - \mu_j^q\right)^* = \sum_{r=q}^{q_j-1} h^{r*} (d\mu_j / dx)^{r*} \text{ if } q_j > q \quad \mathbf{A22s (eqn 5.9b)}$$

where h^{r*} (m^3/mol) are the model layer thicknesses.

If v_{jk} is the stoichiometric coefficient of end-member reaction j in reaction k , the model affinity of reaction is

$$(-\Delta G)_k^* = \sum_j v_{jk} \left(\mu_j^{q_j} - \mu_j^q\right)^*$$

A23 (eqn 5.10)

calculated at boundary q with the reference location for each end-member j at q_j .

Independently, the true reaction affinities $(-\Delta G)_k$ are estimated at a range of P and T from the minerals at their reference locations with the internally consistent dataset of Holland and Powell (1998) and activity models from AX mineral recalculation software. The ratios in true reaction affinities and corresponding model ratios are then compared. A good fit should be found at the P and T of corona formation. Sources of error include the mineral composition data, diffusion modelling, the thermodynamic dataset and also the activity models used. Some ratios are not useful because they are too sensitive to uncertainties in the data.