

Energy-Constrained Open-System Magmatic Processes II: Application of Energy-Constrained Assimilation Fractional Crystallization (EC-AFC) Model to Magmatic Systems

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ABSTRACT

Evidence for open-system magmatic processes is abundant in igneous rocks from most tectonic settings and with ages spanning most of geologic time. Accurately documenting these processes is critical for understanding magma reservoir dynamics, including the processes that lead to compositional diversity in igneous rocks, and for deciphering the thermochemical evolution of the crust and mantle. Quantitative models describing open-system processes such as assimilation-fractional crystallization (AFC) have provided significant insight into all of these, but, nevertheless, suffer from several serious deficiencies. Foremost among these are the absence of energy conservation and the lack of consideration of country rock partial melting. For a magma body undergoing AFC, a new quantitative model, **Energy-Constrained Assimilation Fractional Crystallization (EC-AFC), self-consistently balances energy, species and mass while also tracking compositional variations generated in anatectic melt as country rock undergoes partial melting. EC-AFC represents a significant improvement to existing AFC models for several reasons. First, the inclusion of energy conservation provides a direct and crucial link between thermal parameters and volcanological/geological data. Second, unlike 'classical' AFC that models mass and chemical properties only, EC-AFC models mass, chemical *and* thermal properties of a magma body, thus allowing the energetics of the open-system magma reservoir to be linked to the geochemical evolution. Third, compared to 'classical' AFC models, EC-AFC geochemical trends are distinct, exhibiting non-monotonic behaviors that are directly linked to the effects of energy conservation and country rock partial melting. Comparison of EC-AFC trends with data from natural systems indicates that some of the criteria currently used to demonstrate the efficacy of AFC require modification. Finally, comparison of 'classical' AFC and EC-AFC results for data from well-documented volcanic centers demonstrates that EC-AFC**

does a superior job of tracking the compositional trends, provides a plausible physical context for the process of AFC, and allows geologically relevant predictions to be made about particular magmatic systems.

Key Words: assimilation-fractional crystallization/geochemical model/isotope/magma chamber/trace element

INTRODUCTION

Geochemical, petrologic and petrographic data for igneous rocks provide definitive evidence for the occurrence of open-system processes (e.g., assimilation of anatectic melt, magma recharge, interaction between magma and fluids or magma and hydrothermally altered country rock) in evolving magma bodies. Evidence for such processes has been documented in igneous rocks from most tectonic settings and with ages spanning most of geologic time (Sparks, 1986).

Understanding open-system processes is therefore critical for evaluating magma chamber processes and the thermochemical evolution of the mantle and crust. The significant role that open-system processes play in generating the compositional diversity evident in igneous rocks has been recognized for many years (e.g., Bowen, 1922a, 1922b, 1928), and numerous quantitative treatments have been developed describing the geochemical consequences of these processes (e.g., Allegre and Minster, 1978; Taylor, 1980; DePaolo, 1981; O'Hara and Mathews, 1981; Albarède, 1995). During the last 30 years, significant progress has been made in our understanding of the dynamics of open-system behavior primarily because of improvements in analytical instrumentation, recognition of the critical information provided by trace elements and radiogenic and stable isotopes, and appreciation of the importance of integrating the thermal and chemical characteristics of the magma body with the geologic history of the associated complex.

Despite these great strides, notable deficiencies exist in quantitative treatments of open-system processes. Foremost among these are the lack of a comprehensive accounting of species and mass conservation that is self-consistently coupled to energy conservation and lack of consideration of assimilated compositional variations that result from partial melting of country rock. These deficiencies are especially acute when one notes that the interaction of magma with its host rock is essentially a thermal process. We suggest that geochemical trends resulting from

application of species and mass balance equations may be flawed and may lead to incorrect conclusions about the petrogenetic histories of some igneous rock suites. In recognition of this, we have developed a model of mass, species and energy conservation for a magma body undergoing open-system evolution. In a companion paper (Spera and Bohron, 2000, this volume), we present the conceptual framework of an energy-constrained open-system model and describe the mathematics and assumptions of the Energy-Constrained Assimilation Fractional Crystallization (EC-AFC) formulation (available at <http://magma.geol.ucsb.edu/research/recharge.html>). In this paper, using results of selected EC-AFC simulations, we demonstrate that the EC-AFC formulation is a notable improvement over existing models for several reasons. First, the inclusion of energy conservation provides a direct link between thermal parameters (e.g., initial liquidus and solidus temperatures of magma and country rock) and volcanological and geological data (e.g., depth of the magma reservoir, magma eruption temperature); such a link is critical but generally lacking in current geochemical models. We also show that, compared to 'classical' AFC models (herein defined as models based on only mass and species conservation), distinct geochemical trends may emerge for EC-AFC. Based on a comparison of results from EC-AFC and 'classical' AFC, we show that some of the generalizations made about the process of AFC are in need of modification. As a consequence, some of the broad-scale conclusions about the petrogenetic histories of particular igneous suites may be inaccurate. Finally, because the value of any theoretical model lies in its ability to describe natural systems, in the last part of this paper, we evaluate three published data sets and demonstrate that EC-AFC results do a better job of modeling the observed geochemical trends and of constraining the physiochemical processes associated with AFC. The overarching goal of incorporating energy conservation and country rock partial melting into a quantitative

description of AFC is to provide a more realistic characterization of magmatic processes by explicitly coupling thermal and chemical properties of a magma body. By examining the magma body and country rock as a composite system governed by physiochemical principles, a more comprehensive understanding of the dynamics of magma plumbing systems and the origins of chemical diversity of magmas will emerge.

RESULTS OF SELECTED EC-AFC SIMULATIONS

Here, we present selected results of EC-AFC simulations in order to illustrate physical (e.g., temperature of magma body and country rock, mass of magma body) and chemical characteristics (trace element and isotopic signatures) of two magma body-country rock systems as well as highlight some of the differences between ‘classical’ AFC and EC-AFC results.

Incorporated into this analysis are results of sensitivity tests that illustrate examples of potential compositional variability introduced by independently varying particular thermal or chemical input parameters. Although a complete sensitivity analysis is not presented, any and all permutations of interest can be easily and rapidly handled by the EC-AFC program. The two composite systems are a ‘standard’ upper crustal case and a ‘standard’ lower crustal case (Table 1). The upper crustal example is illustrative of basaltic magma intruded at a liquidus of 1280°C into upper crust of ambient temperature 300°C (depth ~10 km). The composition of the crust is roughly granitic, with a liquidus temperature of 1000°C, and the implied water content of anatectic melt is a few per cent by mass. The local solidus temperature, T_s , is 900°C. The geochemical parameters correspond to values typical of upper crust (e.g., Taylor and McLennan, 1985). The ‘standard’ lower crustal case represents intrusion of more primitive basaltic magma with a liquidus of 1320°C into lower crust of ambient temperature 600°C (depth ~20 km). The crust is mafic, with a liquidus temperature of 1100°C. The local solidus temperature is 950°C.

The geochemical parameters correspond to typical trace element and isotopic values for lower crust (e.g., Taylor and McLennan, 1985). For the purposes of comparison, $T_{eq} = 980^{\circ}\text{C}$ for both cases. In both, melt productivity is a linear function of temperature for magma and country rock; that is, $f_m(T_m) = (T - T_s)/(T_{l,m} - T_s)$ and $f_a(T_a) = (T - T_s)/(T_{l,a} - T_s)$ (for explanation of nomenclature, see Table 1, Spera and Bohrson, 2000, this volume). Isobaric specific heats, heat of fusion and heat of crystallization for magma and country rock were computed from data in Tables 2 and 3 of Spera and Bohrson (2000, this volume).

Physical characteristics of the magma body-country rock system

The EC-AFC formulation permits an accounting of thermal and mass characteristics during the AFC ‘event’, including the temperatures of the magma body and country rock, the masses of melt and cumulates in the magma body, and the mass of anatectic melt assimilated into the magma body. Such parameters are critical for developing an accurate understanding of the dynamics of magma reservoirs. For the ‘standard’ upper crustal case, the trajectory in T_m - T_a coordinates is shown in Fig. 1a. Sensible and latent heat liberated by the magma as it cools and crystallizes goes into sensible heating of the country rock. For each degree drop in melt temperature (T_m), the *average* temperature of country rock (T_a) increases by $\sim 3.5^{\circ}\text{C}$. During this stage of the AFC ‘event’, on average, anatectic melt is not present because $T_a < T_s$, and the geochemical evolution of the magma body is driven by fractional crystallization. For $T_a < T_s$, the fraction of melt (M_m) decreases as cumulates form. Unlike ‘classical’ models in which energy conservation is ignored however, M_m is not a monotonically decreasing function of T_m . At $T_a > T_s$, because of the addition of anatectic melt, M_m can *increase* as T_m continues to drop towards T_{eq} (Fig. 1a). Also, at $T_a > T_s$, T_a rises more slowly due to the enthalpy requirements of anatexis (Fig. 1a). The mass of anatectic melt delivered to the magma body (M_a^*) and mass of cumulates

removed by fractional crystallization (M_c) are portrayed in Fig. 1b. When $T_a < T_s$, (no anatectic melt), the ratio of the mass of anatectic melt to the mass of cumulates (M_a^*/M_c) is zero but increases to ~ 0.7 as country rock heats up to T_{eq} (Fig. 1c). This variation should be noted. Recall that in ‘classical’ AFC, M_a^*/M_c (the parameter r) is a *constant*. Trends for the ‘standard’ lower crustal case (Fig. 1a, b, c) are qualitatively similar to those of the upper crustal case, although the ratio M_a^*/M_c has a smaller range (0 – 0.35) throughout the AFC ‘event’, reflecting both the higher solidus and the greater fusion enthalpy of lower compared to upper crust. One additional example is illustrated where all parameters are the same as those of the ‘standard’ upper crustal case except that the melt production curves for both magma and country rock are taken as nonlinear functions of temperature (referred to as ‘nonlinear’ upper crustal case; Fig. 2). The distinct T-melt fraction relations introduce differences in the mass of anatectic melt assimilated and the magma–country rock temperature profile (Fig. 1a, b, c). In addition, as noted below, distinct differences in composition also result.

Isotope-element and element-element trends

Geochemical trends unlike those associated with ‘classical’ AFC are well illustrated by examining Sr concentration ($[Sr]$) *versus* $^{87}Sr/^{86}Sr$ trends for three EC-AFC cases (Fig. 3a). The first and second are the ‘standard’ upper crustal case and the ‘nonlinear’ upper crustal case, both of which model Sr as compatible in magma and country rock (Table 1a; D_m, D_a for both = 1.5). The third illustrates the ‘standard’ lower crustal case, where country rock Sr is modeled to behave incompatibly (Table 1b; $D_a = 0.05$). Fig. 3a shows that in all cases, $[Sr]$ initially decreases while no change in $^{87}Sr/^{86}Sr$ occurs, leading to a flat trajectory in element-isotope space. This is because no anatectic melt forms as country rock heats up from its initial

temperature (300 °C, 600 °C) to its solidus (900 °C, 950 °C); during this stage, the geochemical evolution of the magma body is characterized by only fractional crystallization. Although assimilation has not affected the geochemistry of the magma body, heat is being transferred from the magma body to country rock. Thus, although ‘classical’ AFC solutions would never associate this part of the path with AFC, it is an integral part of the process. Once country rock reaches its solidus, partial melt is generated and mixed into the magma body. When partial melting begins, in the upper crustal cases, [Sr] of contaminated magma continues to decrease while $^{87}\text{Sr}/^{86}\text{Sr}$ becomes more radiogenic, consistent with the compatible nature of Sr in both country rock and magma and with incorporation of more radiogenic assimilate. Note that although the patterns for the ‘standard’ and ‘nonlinear’ upper crustal cases are similar, Fig. 3a reveals that for the ‘nonlinear’ case, $^{87}\text{Sr}/^{86}\text{Sr}$ and [Sr] are equal to 0.7200 and 310 ppm at $T_{\text{eq}} = 980^\circ\text{C}$, whereas for the ‘standard’ case, the values are 0.7135 and 318 ppm, respectively. These differences underscore the strong dependence of geochemical path on parameters included in the EC-AFC formulation; temperature–melt fraction relations as well as other thermodynamic parameters influence the extent and characteristics of magma contamination. Thus, one of the single most important conclusions of this work is that the energetics of petrologic processes are a profound constraint that must be applied in order to study complex AFC phenomena; AFC without self-consistent application of energy conservation is like an automobile without an engine.

For the ‘standard’ lower crustal case, at $T_a > T_s$, [Sr] *increases* while $^{87}\text{Sr}/^{86}\text{Sr}$ increases because during fractional melting of an incompatible element, the smallest (lowest temperature) melt fractions have very high Sr concentrations (Fig. 3b). Thus, because of the highly incompatible behavior of Sr in the lower crustal case, more Sr is being added to the contaminated magma by assimilation than is being removed by fractional crystallization. Therefore, both [Sr]

and $^{87}\text{Sr}/^{86}\text{Sr}$ increase. By ~10% melting of country rock ($F = 0.10$), [Sr] in anatectic melt is less than that in the magma body itself (~880 ppm Sr in contaminated magma body when country rock is melted 10%), and therefore, the Sr concentration in the contaminated magma decreases in response to fractional crystallization and the 'dilution' effect of adding low-Sr anatectic melt. At this stage, because so little assimilated Sr is being contributed to contaminated magma, $^{87}\text{Sr}/^{86}\text{Sr}$ changes very little. This part of the modeled EC-AFC process is reflected in the relatively flat trajectory where $^{87}\text{Sr}/^{86}\text{Sr}$ is ~0.709 and [Sr] decreases from ~880 ppm to ~530 ppm (Fig. 3a).

Despite the lack of variation in $^{87}\text{Sr}/^{86}\text{Sr}$, it is important to keep in mind that assimilation is still ongoing. Because such a trajectory can not be modeled by 'classical' AFC, the lack of variation in some isotope ratios may lead to the misinterpretation that the associated magmas are the products of dominantly closed-system fractional crystallization. For example, some silicic volcanic suites that have isotope signatures that show little variation with indices of differentiation have been described as the products of dominantly fractional crystallization (i.e., low rates of assimilation, Grunder, 1992; Wark, 1991). The critical point is that some EC-AFC simulations predict only minor variations in some isotope ratios during the later stages of the AFC process when the total mass of assimilated material reaches its maximum, and suites of differentiated rocks with such signatures should be evaluated with this possibility in mind. Because of the abundance of O in most magmas, $^{18}\text{O}/^{16}\text{O}$ typically does not exhibit a flat trajectory at this stage in the AFC 'event', provided there is a contrast between the oxygen isotope signatures of magma and country rock; for this reason characterizing oxygen isotopes in some suites of igneous rocks is particularly important.

Model results calculated using equations from DePaolo (1981) highlight the remarkable and very significant differences between 'classical' AFC and EC-AFC (Fig. 3a). Where appropriate,

input parameters are the same, and r is estimated based on an average M_a^*/M_c . Among the most important differences are the lack of a flat Sr- $^{87}\text{Sr}/^{86}\text{Sr}$ trajectory at ~ 0.7035 and the lack of the non-monotonic trajectory illustrated by the lower crustal EC-AFC model.

Another interesting pattern in Sr isotope-[Sr] space is revealed by examining cases where Sr in both magma and country rock behaves compatibly, but [Sr] in the country rock is similar to or greater than that in the uncontaminated, unfractionated magma. Three cases are shown where *EC-AFC, upper* represents the ‘standard’ upper crustal case, and *EC-AFC, 700* and *EC-AFC, 1000* are the ‘standard’ upper crustal case but with the initial country rock Sr concentration, Sr_a^0 , equal to 700 ppm and 1000 ppm, respectively. Once wallrock partial melting begins, [Sr] in the ‘standard’ upper crustal case decreases as magma temperature drops (Fig. 4a). [Sr] in *EC-AFC, 700* initially decreases slightly but then increases. The changes in concentration reflect the effect that fractional melting has on a compatible element (Fig. 4b). At small degrees of partial melting, relatively little Sr is liberated from country rock into the anatectic melt. As the degree of melting increases, more Sr is partitioned into anatectic melt, until eventually, in *EC-AFC, 700*, proportionally more is being added by assimilation than is being removed by fractional crystallization. In *EC-AFC, 1000*, [Sr] increases as T_m decreases, reflecting the effect of both fractional melting and the high Sr_a^0 . In this example, the high Sr_a^0 allows the contaminated magma $^{87}\text{Sr}/^{86}\text{Sr}$ to achieve relatively radiogenic values at fairly high concentrations of Sr, despite a large amount of fractional crystallization that has occurred ($M_c = \sim 0.79$ at T_{eq} for all three cases). For similar input parameters, positive correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and [Sr] can not be produced by ‘classical’ AFC models (Fig. 4a) because partial melting of country rock is not accommodated.

The behavior of an element, such as Nd, that may be incompatible in both magma and country rock is illustrated in Fig. 5, which depicts results for the ‘standard’ upper, ‘nonlinear’ upper and ‘standard’ lower crustal cases. For all, the Nd concentration ([Nd]) initially increases while $^{143}\text{Nd}/^{144}\text{Nd}$ remains unchanged, reflecting heating of country rock to T_s . When anatexis begins, [Nd] increases as $^{143}\text{Nd}/^{144}\text{Nd}$ decreases, consistent with its incompatible behavior in both magma and country rock and addition of anatectic melt that is characterized by a less radiogenic Nd isotope signature. The lower crustal case has a more protracted period of wallrock heating (and fractional crystallization only) because of its higher T_s , and therefore it has higher [Nd] when anatexis commences. Fractional melting eventually depletes Nd from the country rock residue. Therefore, anatectic melt has very little Nd, and its concentration in the contaminated magma decreases despite Nd behaving incompatibly during fractional crystallization. In the case of both upper crustal examples, the relatively flat element-isotope trajectory at low $^{143}\text{Nd}/^{144}\text{Nd}$ is due to the small amount of assimilant Nd that is being added to contaminated magma (Fig. 5); in the lower crustal case, T_{eq} is reached before this phenomenon occurs. Note again that the ‘standard’ and the ‘nonlinear’ upper crustal cases exhibit different [Nd]- $^{143}\text{Nd}/^{144}\text{Nd}$ characteristics. Also, the non-monotonic trends are not generated by ‘classical’ AFC models (Fig. 5).

The complex geochemical trends illustrated above are fingerprints of the EC-AFC process, reflecting the constraint of energy conservation and the effects of partial melting. In particular, the lack of variation in isotopic ratio of a trace element as its concentration varies is a tell-tale signal of an EC-AFC process and contrasts with ‘classical’ AFC trends where monotonic trends are typical. The distinctions in EC-AFC *versus* ‘classical’ AFC trends (Fig. 3a, 4a and 5) underscore an important point. In some studies, AFC has been rejected because observed data

trends are not consistent with modeled ‘classical’ AFC trends (e.g., Taylor, 1980; Carlson et al., 1981; Lum et al., 1989; Kempton et al., 1991, Blichert-Toft et al., 1992). It is critical to appreciate that the ability to determine whether AFC has occurred depends—at least in part—on the formulation used to quantify the process. A concrete example of this involves the use of $1/\text{Sr}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ plots. Because a monotonic $1/\text{Sr}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ trend is predicted by ‘classical’ AFC models, its absence in data trends from particular volcanic centers has been interpreted as evidence against AFC (e.g., Kempton et al., 1991; Lum et al., 1989; Fitton et al., 1991). It is clear, however, that such a trend will not result in the cases illustrated in Fig. 3a and 4a, and yet, these clearly are data trends that reflect one possible mode of AFC. Another example of model-dependent results involves the interpretation that the most differentiated sample is also the most contaminated sample. In ‘classical’ AFC, the most differentiated sample is typically regarded as that with the highest concentration of a particular incompatible trace element and that has undergone the greatest amount of fractional crystallization. The extent of contamination is most commonly assessed with radiogenic or stable isotope ratios, with the most contaminated being that sample with an isotope signature most like that of country rock. For AFC to be considered as an important process, many workers require that a good correlation between these two exist (e.g., Carlson et al., 1981; Chazot and Bertrand, 1993; Mason et al., 1996; Marsh, 1989). This filter has developed primarily because solutions to ‘classical’ AFC equations yield monotonic changes in incompatible trace element concentration versus isotope ratio. EC-AFC demonstrates that this monotonic correlation is not always present. For all EC-AFC simulations, magma at T_{eq} has assimilated the largest mass of anatectic melt, but as illustrated in Fig. 5, magma with the highest [Nd] has not assimilated the most anatectic melt. The element-element patterns shown in Fig. 6a and 6b further emphasize this point. Magma that has assimilated the largest mass of anatectic

melt does not have the highest concentration of Th or Nd (both modeled as incompatible in magma and country rock). Based on a comparison with trends calculated using 'classical' AFC equations (Fig. 6), the non-monotonic EC-AFC trends shown for Nd-Sr and Nd-Th would either not be interpreted as AFC trends or several different contaminants would be invoked to explain the range of abundances. Thus, conclusions regarding the importance of AFC based on the absence of simple correlation between degree of differentiation and amount of contamination may not be correct; indeed the assumption that the sample with the highest concentration of incompatible element is the most differentiated (e.g., has undergone the most fractional crystallization) is not necessarily correct. The critical point is that while comparison between data and quantitative models forms a backbone of geochemical and petrological studies, the examples described here illustrate that potential misinterpretations may arise in model-dependent studies. In view of the very distinct differences that can occur between EC-AFC and 'classical' AFC geochemical trends, some case studies in which the process of AFC has been dismissed may merit reexamination.

Mass balance arguments

Mass balance arguments have been used to suggest that relatively radiogenic Sr isotope signatures of basalts can not result from the process of AFC because addition of the mass of (differentiated) assimilant required to generate relatively radiogenic isotope signatures would yield magmas that are no longer basaltic. This argument has been used in interpretations of the origin(s) of extension-related basalts in the Western US (Lum et al., 1989; Kempton et al., 1991). For the 'standard' lower crustal case, with the addition of a mass of assimilant that is ~10% of the total mass of original magma ($M_a^*/M_o = 0.1$), $^{87}\text{Sr}/^{86}\text{Sr}$ climbs to >0.708 from its initial value

of 0.7035 and [Sr] increases to ~880 ppm (Fig. 7a, 7b). Depending on the composition of the assimilant, the addition of such a small mass may not significantly change the major element composition of the magma body. For example, addition of 10% assimilant with 70 wt. % SiO₂ would only change SiO₂ of a basalt with 50 wt. % by roughly 2 wt. %. Certainly, a magma with 52 wt. % and a Sr concentration of ~880 ppm would be considered “basaltic.” A ‘classical’ AFC calculation using the same input parameters, where appropriate, requires an r of ~0.45 to achieve ⁸⁷Sr/⁸⁶Sr of ~0.7084 at a similar degree of crystallization ($M_c = \sim 0.8$). Compared to the EC-AFC results, ‘classical’ AFC requires addition of a factor of ~3.5 more assimilant by mass. Although the effect on composition is strongly dependent on input parameters, this EC-AFC result indicates that relatively radiogenic Sr isotope signatures can be achieved through addition of small amounts of crustal assimilant that may not drastically alter the major element composition of the magma body. Mass balance arguments based on ‘classical’ AFC results may overestimate the required amount of assimilant and thereby lead to incorrect conclusions regarding the origin of ‘enriched’ signatures in basalts.

Arguments have also been made about the ability of the process of AFC to affect magmas characterized by high Sr concentrations (Lum et al., 1989; Kempton et al., 1991) or other trace elements (i.e., magmas with high abundances of incompatible trace element may be considered insensitive to AFC; e.g., Davidson et al., 1990). Fig. 8a, b illustrate results of three upper crustal simulations; *EC-AFC, upper* is the ‘standard’ upper crustal model whereas *EC-AFC, 233* and *EC-AFC, 175* represent the ‘standard’ upper crustal model but with Sr_a^o of 233 ppm and 175 ppm, respectively. These values were chosen to reflect Sr_m^o/Sr_a^o of 2/1, 3/1 and 4/1, respectively. Modeled with these parameters, with less than 20% addition of assimilant relative to the original mass of magma ($M_a^*/M_o = 0.2$), the contaminated magma is characterized by [Sr] that exceeds

300 ppm and by $^{87}\text{Sr}/^{86}\text{Sr}$ that is greater than ~ 0.7055 (Fig. 8a, b). For the ‘standard’ lower crustal case, where Sr is incompatible in the country rock and $\text{Sr}_m^0/\text{Sr}_a^0$ is 2/1, 3/1 or 4/1, $^{87}\text{Sr}/^{86}\text{Sr}$ of contaminated magma is 0.708 and $[\text{Sr}] > 700$ ppm for just 10% addition of assimilate (Fig. 8c, 8d). Thus, despite relatively high $\text{Sr}_m^0/\text{Sr}_a^0$, contaminated magma Sr isotope signatures can be profoundly changed with addition of a relatively small mass (20% of total mass of original magma) of assimilate.

Fig. 9 shows that there is not necessarily a simple correlation between mass of anatectic melt assimilated (M_a^*/M_o) and the geochemical signature of the magma body. This is in distinct contrast to ‘classical’ AFC results that predict that, all other parameters being equal, the more mass assimilated (higher r), the more crust-like the isotope ratios will be (e.g., Fig. 3a and 5a). All other parameters being equal in the ‘standard’ upper crustal case ($T_{\text{eq}} = 980^\circ\text{C}$), different T_{eq} (950°C , 920°C , Fig. 9) yield differences in the mass of anatectic melt assimilated. The 920°C case involves the largest mass of country rock, M_a^0 , but the smallest proportion of assimilate, M_a^*/M_o . This is because a T_{eq} of 920°C is closest to T_s , and therefore, at T_{eq} , $f_a(T_a)$ is the smallest of the three examples. Energy heats up a large mass of country rock but only melts it to a small degree. In contrast, the 980°C case has the smallest M_a^0 , the largest $f_a(T)$, and the largest M_a^*/M_o . Fig. 9b shows that the 920°C example produces magma with the most contaminated Sr isotope signature (~ 0.7160), whereas the 980°C example is characterized by magma with the least contaminated Sr isotope signature (~ 0.7140). For the 920°C case, assimilation initiates at the lowest T_m because M_a^0 is the largest. When country rock partial melting commences, magma in the 920°C example has undergone the most fractional crystallization, and as a consequence, $[\text{Sr}]$ in the magma body is lowest of the three cases (~ 250 ppm, Fig. 9a). Country rock Sr makes up a greater proportion of Sr in the contaminated magma body, and therefore, $^{87}\text{Sr}/^{86}\text{Sr}$ is the

most radiogenic. Nd exhibits different behavior. The 920°C case yields magma with the highest [Nd] (Fig. 9c) whereas the most contaminated (crustal) Nd isotope signature is the 950°C case (Fig. 9d). The explanation for this lies in the complex interplay between the incompatible behavior of Nd in both magma and country rock and the effects of fractional melting.

Variations in compositionally-dependent thermal parameters

It is well-known that liquidus and solidus temperatures, specific heats, and heats of crystallization and fusion are broadly dependent on composition. Changes in any of these parameters have consequences on EC-AFC chemical trends. For example, for the ‘standard’ upper crustal case where all other parameters are fixed, raising the liquidus temperature of country rock by 200°C (i.e., $T_{1,a} = 1200^\circ\text{C}$, more mafic country rock) decreases the proportion of anatectic melt that is incorporated (M_a^*/M_o) from ~0.55 to ~0.21. More energy is required to reach the solidus temperature and initiate anatexis because the total mass of country rock (M_a^o) involved in the AFC ‘event’ is larger, which leads to a smaller M_a^*/M_o . In this case, compared to the ‘standard’ upper crustal case, at T_{eq} , the magma body displays a less contaminated Sr isotope signature and a similar Nd isotope signature (Fig. 10a, 10b). In contrast, raising the liquidus and initial temperatures of uncontaminated magma ($T_{1,m}$, $T_m^o = 1500^\circ\text{C}$), which is equivalent to intruding a more mafic magma, yields a higher M_a^*/M_o (Fig. 10a, 10b). More heat is generated by the magma body as it cools and crystallizes, and therefore more heat is available for anatexis, which leads to a larger M_a^*/M_o (~0.85). Compared to the ‘standard’ upper crustal case, both Sr and Nd isotopes are more crust-like.

Changing the solidus temperature also influences the chemical evolution of the magma body. Fig. 11 illustrates results of two cases, the ‘standard’ upper crustal case and a case in which all

other parameters are equal but the solidus is reduced to 800°C. For this comparison, the lower solidus allows assimilation to begin at a higher T_m . Despite assimilating very similar total proportions of anatectic melt ('standard' $M_a^*/M_m^0 = 0.55$ versus 800°C case = 0.54), the 'standard' case ultimately yields magma characterized by more crustal isotope signatures. For $T_s = 800^\circ\text{C}$, because assimilation initiates at a higher T_m , less fractional crystallization has occurred. [Sr] is therefore higher when assimilation commences, and because of this, at T_{eq} , magma is characterized by a less radiogenic Sr isotope signature (Fig. 11a). Compared to the 'standard' case, [Nd] in the 800°C case is less enriched when assimilation commences (Fig. 11b), and this allows the 'dilution' effect to occur at a higher T_m . Therefore, $^{143}\text{Nd}/^{144}\text{Nd}$ becomes relatively constant at a less crustal value compared to the 'standard' upper crustal case.

Variations in parameters that reflect initial thermal conditions of country rock

The initial temperature of the country rock (T_a^0), in part, reflects the ambient geothermal gradient (Spera and Bohrsen, 2000, this volume). Fig. 12 illustrates results of two cases, the 'standard' upper crustal case and the same but with the T_a^0 elevated to 600°C. A possible scenario to explain this higher temperature would be regional heating of upper crust due to mafic underplating. We stress that the 600°C case discussed here is different from the 'standard' lower crustal case where thermal and compositional parameters have been selected to reflect assimilation of more mafic lower crust. The proportion of anatectic melt that is assimilated is greater in the 600°C case ($M_a^*/M_o = \sim 0.85$) than in the 'standard' case ($M_a^*/M_o = \sim 0.55$). Because less heat is required to elevate country rock to T_s , assimilation commences at a higher T_m . The larger M_a^*/M_o associated with the 600°C case, compared to the 'standard' case, yields more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 12a) and less radiogenic (more crustal) $^{143}\text{Nd}/^{144}\text{Nd}$ (Fig. 12b).

The 600°C case also provides evidence that ratios of mass of assimilated melt to mass of cumulates removed (equivalent to r , DePaolo, 1981) can exceed unity: at T_{eq} , M_a^*/M_c for the 600°C case is 1.1. Based on energy conservation, there is no justification for arbitrarily limiting this parameter to less than unity.

Summary

The results presented in this section clearly demonstrate two critical points about EC-AFC. (1) Thermochemical parameters that characterize magma bodies are complex and interconnected; inclusion of energetic constraints in modeling the geochemistry of rocks influenced by complex AFC processes is therefore an absolute necessity. (2) The incorporation of energy conservation and country rock anatexis into a formulation of AFC yields geochemical trends that can be quite distinct from those predicted by ‘classical’ AFC; therefore, some of the generalizations made about the process of AFC merit reevaluation, which, in turns indicates that some data sets may need to be reexamined.

APPLICATION OF EC-AFC TO NATURAL SYSTEMS

A critical test of the applicability of the EC-AFC formulation is its ability to explain data from natural systems. Below, results of EC-AFC simulations are presented for geochemical data from three volcanic systems that are well-documented with respect to their eruptive histories and petrographic and geochemical characteristics. Each of the associated magmatic systems was affected by AFC, and particular data trends for each display non-monotonic trace element-isotope behavior. Of particular note in each data set is the Sr *versus* $^{87}\text{Sr}/^{86}\text{Sr}$ trend. From our comparison of ‘classical’ *versus* EC-AFC modeling results, we conclude that, in general, EC-

AFC does a superior job of modeling the compositional evolution, and it allows geologically relevant predictions to be made about the magmatic systems.

Mafic to intermediate volcanic rocks from the Long Valley caldera and Devil's Postpile National Monument, eastern, CA

Abundant mafic to silicic volcanism characterizes the region near Long Valley caldera, the site of caldera collapse associated with the eruption of the 0.73 Ma Bishop Tuff. Of specific interest in this region is a suite of Quaternary (0.151–0.415 Ma; Vogel et al., 1994) basalt to trachyandesite volcanic rocks exposed in the west moat of Long Valley caldera and in Devil's Postpile National Monument, which is located several kilometers to the west of the caldera. Vogel et al. (1994) analyzed continuous core from the Inyo-4 drill hole, located in the west moat, for major and trace elements. Cousens (1996) analyzed surface samples from the west moat and Devil's Postpile area for major and trace elements. In addition, Cousens analyzed the surface and drill hole samples for Sr, Nd, and Pb isotopes. Typically, samples from both suites are phyrlic (1–20 vol. %), with plagioclase>olivine>clinopyroxene (Cousens, 1996). SiO₂ abundances range from 48 to 58 wt. %, and MgO ranges from 2.6 to 7.5 wt. %. Drill core samples, which define a smooth trend of more differentiated compositions up-section, are interpreted to be products of periodic eruption of a continuously evolving magma body (Vogel et al., 1994). Vogel et al. (1994) suggest that differentiation of the oldest, most mafic lavas was dominated by fractional crystallization whereas the chemical evolution of younger, more evolved lavas was controlled by assimilation. Detailed trace element and isotopic work by Cousens (1996) supports this interpretation. Sr isotope ratios (0.70591–0.70635) increase with increasing SiO₂ abundance, and the stratigraphically lowest samples in the Inyo-4 drill core have the least radiogenic Sr isotope

signatures. ‘Classical’ AFC models suggest that country rock similar in composition to locally sampled Sierran granitoids was assimilated during fractional crystallization of mafic magma (Cousens, 1996). However, trace element and isotopic variations among the Moat-Postpile lavas can not be explained by a single ‘classical’ AFC model. Based on ‘classical’ AFC results presented in Cousens (1996), multiple trends reflecting relatively large variations in r (0.25 – 2) are required, and Cousens also suggests involvement of compositionally distinct parental magmas and chemically heterogeneous country rock.

One of the more interesting element-isotope trends for the Moat-Postpile lavas is [Sr]- $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 13). The data comprise a three part trend in which the most mafic samples cluster at the least radiogenic Sr isotope values (~ 0.70595) but range from ~ 750 to 875 ppm Sr, intermediate composition samples exhibit increasing [Sr] with increasing $^{87}\text{Sr}/^{86}\text{Sr}$, and the most evolved samples show a relatively small range of $^{87}\text{Sr}/^{86}\text{Sr}$ at lower [Sr]. This non-monotonic trend can not be modeled by a single ‘classical’ AFC trend. The entire range of compositions requires very different conditions, including different r values (e.g., 0.2-0.8) and distinctly different mineral-melt partition coefficients for Sr (e.g., 0.33-1.5; Fig. 13). Consistent with the conclusion of Cousens (1996), the observation that plagioclase is abundant in most of the samples suggests that Sr behaves compatibly during crystal fractionation; this indicates that the trend where $D_{\text{Sr}} = 0.33$ is not realistic. Using ‘classical’ AFC equations, it is therefore impossible to generate the positive [Sr]- $^{87}\text{Sr}/^{86}\text{Sr}$ trend evident among some of the samples.

Reasonable input parameters (Table 2) yield an EC-AFC trend that is strikingly similar to that formed by the Moat-Postpile data; the model suggests that AFC occurred in the middle crust, where partial melts of the less silicic roots of Sierran plutons may have contaminated the magma body. Several specific aspects of the EC-AFC results are noteworthy. First, the suggestion of

Vogel et al. (1994) that the oldest lavas seem to be related dominantly by fractional crystallization, an observation that is confirmed by the Sr isotope data, is supported by the EC-AFC model. In EC-AFC, this fractionation-dominated stage represents heating of country rock from T_a^o to T_s . Because Sr appears to have behaved compatibly in the magma body during fractional crystallization (Cousens, 1996), the [Sr]- $^{87}\text{Sr}/^{86}\text{Sr}$ trajectory is consistent with Sr behaving incompatibly during country rock partial melting. The modeled country rock Sr isotope ratio is similar to that reported by Cousens (1996) for local Sierran granitoids, although the modeled initial and liquidus temperatures of the assimilant (550°C and 1100°C, respectively) suggest that the country rock may be the deeper, less silicic (granodioritic to dioritic) roots of a Sierran-type pluton. Second, major element modeling (Vogel et al., 1994) suggests that some of the youngest samples from the Inyo-4 drill hole experienced significant assimilation. Despite this, these samples exhibit a relatively narrow range of $^{87}\text{Sr}/^{86}\text{Sr}$ (0.70621-0.70638). A rhyodacite sampled in the Devil's Postpile area (Cousens, 1996) also has $^{87}\text{Sr}/^{86}\text{Sr}$ in this range (0.70636, Fig. 13). Such small variation in Sr isotopes among the most evolved samples, despite evidence for assimilation, is difficult to reconcile with 'classical' AFC models because [Sr]- $^{87}\text{Sr}/^{86}\text{Sr}$ trajectories typically do not flatten out (Fig. 13). The flat trajectory at $^{87}\text{Sr}/^{86}\text{Sr}$ of ~0.70632 potentially reflects the dilution effect that causes little change in $^{87}\text{Sr}/^{86}\text{Sr}$ to occur. Finally, because the magmatic system associated with the Moat-Postpile samples is hypothesized to be a single, continuously evolving chamber and the relative chronology of eruption of the lavas is so well known (Vogel et al., 1994), this case study provides an excellent test of the potential application of EC-AFC. Consistent with observations, the model results predict that the first magmas to be erupted will be the least evolved and least contaminated whereas the last magmas to be erupted will be the most evolved and most contaminated. Because this prediction as well as

the others discussed above are consistent with observed data, we suggest that this EC-AFC model more closely describes the conditions under which AFC occurred. We also stress that the model results make specific predictions about the system (e.g., the composition and thermal characteristics of country rock) that can be tested with further examination of geochemical and geological data.

Columbia River Basalts

Between ~6 and 17 Ma, the Columbia River Basalts (CRB) erupted in what are now the states of Oregon, Washington, and Idaho, USA. Because of their total volume (~173,000 km³), tholeiitic character, and rapid eruption rates (>91% of the volume erupted in < 2 my; Hooper and Hawkesworth, 1992), the CRB are considered a small but typical example of a continental flood basalt (Hooper and Hawkesworth, 1992). Based on the recently revised stratigraphic nomenclature of Hooper and Hawkesworth (1992), the CRB are divided into the subgroups Clarkston and Saddle Mountains Basalts. The Clarkston Basalt, which comprises >97% of the volume of the CRB and was erupted between 14.5 and 17.2 Ma, includes the Imnaha, Grande Ronde, Eckler Mountain, and Wanapum Formations. The Saddle Mountain Basalt includes volumetrically insignificant (<1.5 %) basalts that range in age from <14.5 to ~6 Ma.

Most CRB are dominantly aphyric, but it is likely that plagioclase, olivine and pyroxene were liquidus phases, with plagioclase being the dominant constituent of the cumulate assemblage. The lavas are classified as tholeiitic basalt, although SiO₂ and MgO (wt. %) range from 48-57 and 2.5-7.9, respectively. Sr (0.7034-0.7145) and Nd (0.5121-0.5130) isotope ratios vary considerably among all formations of the CRB, although the volumetrically significant Imnaha and Grande Ronde Formations exhibit more limited ranges (Sr isotopes: 0.7035-0.7058; Nd

isotopes: 0.51261-0.51304; Hooper and Hawkesworth, 1992; Carlson et al., 1981). Of particular note is the observation that some CRB have Nd isotope ratios similar to that of present-day chondrite (DePaolo and Wasserburg, 1976a, 1976b), although these samples are among the more fractionated of the CRB (Carlson et al., 1981)

The observation that some CRB samples, as well as a limited number of samples from other continental flood basalts, have $\epsilon_{Nd} = 0$ has led to the suggestion that the source of continental flood basalts was primordial undifferentiated mantle (DePaolo and Wasserburg, 1976a, 1976b). Carlson et al. (1981) dispute this conclusion, citing the isotopic heterogeneity evident in the CRB, an apparent correlation between geographic location and isotope signature, and the observation that those samples with $\epsilon_{Nd} = 0$ are among the most differentiated. Carlson et al. (1981) suggest that involvement of continental crust was responsible for some of the isotopic variation observed in the CRB. Although controversy ensued about the petrogenesis of the CRB and other continental flood basalts, the weight of the evidence seems to favor involvement of a crustal component to explain some of the isotopic heterogeneity. By comparing 'classical' AFC modeling results with their data, Carlson et al. (1981) conclude that AFC explains some of the CRB data, and the most likely assimilant is sialic continental crust, perhaps of Precambrian age. Specifically, the Grande Ronde basalts, which represent the dominant volume of the CRB, are described by AFC whereas the lack of "coupled trace element-isotopic variation" (Carlson et al., 1981) precludes an origin by assimilation of evolved crust during fractional crystallization for the Innaha basalts.

The Sr *versus* $^{87}\text{Sr}/^{86}\text{Sr}$ trend for the Grande Ronde and Innaha basalts, which comprise ~91 volume % of the CRB, may shed light on the origin of some of the isotopic heterogeneity in these formations. Data from some Innaha basalts (Hooper and Hawkesworth, 1992; Carlson et

al., 1981) exhibit a trend of relatively constant $^{87}\text{Sr}/^{86}\text{Sr}$ over a range of [Sr] from ~400-260 ppm. For basalts of both the Grande Ronde and Imnaha, more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ (~0.704-0.705) is coupled with higher [Sr] (~250-375 ppm), although the most radiogenic samples (0.7055) do not have the highest [Sr] (~320 ppm) (Fig. 14). Carlson et al. (1981) require multiple 'classical' AFC trends and particularly note the inability of 'classical' AFC to explain the Imnaha samples. Reasonable EC-AFC parameters (Table 3) yield Sr- $^{87}\text{Sr}/^{86}\text{Sr}$ trends that encompass most of the range displayed by the Imnaha and Grande Ronde basalts and suggest that the associated magma body underwent AFC in the middle to lower crust. The assimilant was probably intermediate to mafic crust. The EC-AFC results can explain the relatively flat element-isotope trend as well as the increasing [Sr] with increasing $^{87}\text{Sr}/^{86}\text{Sr}$ in the CRB data (Fig. 14). The positive Sr- $^{87}\text{Sr}/^{86}\text{Sr}$ trend evident in these CRB samples can not be explained by a 'classical' AFC model unless Sr is modeled to behave incompatibly during fractional crystallization (e.g., AFC₂ trend, Fig. 14). Because evidence exists to the contrary (i.e., plagioclase as a dominant phase, Carlson et al., 1981), we emphasize that 'classical' AFC models are totally inadequate to describe these trends. In the EC-AFC model, Sr is modeled as compatible in the magma, consistent with the dominance of plagioclase as a liquidus phase (Carlson et al., 1981), whereas Sr is modeled as incompatible during melting of country rock. This may be consistent with lower crustal temperatures ($T_a^\circ = 600^\circ\text{C}$) as well as an assimilant liquidus temperature ($T_{1,a} = 1150^\circ\text{C}$) that is indicative of intermediate to mafic composition. In addition, the Sr isotope ratio required for EC-AFC assimilant is much less radiogenic than that modeled by Carlson et al. (1981); the lower Rb/Sr of less silicic rock would lead to less radiogenic time-integrated $^{87}\text{Sr}/^{86}\text{Sr}$. No single EC-AFC model can explain all of the Grande Ronde and Imnaha data (Fig. 14, Table 3), suggesting the country rock associated with CRB magma chambers is heterogeneous in both its elemental and isotopic

character. Similarly, the isotope ratios of the least differentiated basalts are also heterogeneous, suggesting that either the parental magmas were compositionally variable or that the least differentiated samples experienced some open-system processing that resulted in heterogeneous Sr isotopic signatures. Although the total mass of assimilant involved is ~44% of the total volume of original magma, simulations show that most of the contamination occurred with inclusion of only ~20% of the total volume of original magma. Thus, for the more extreme compositions, relatively large amounts of assimilant are required, whereas the dominant proportion of the Grande Ronde and Imnaha basalts can be explained by assimilation of small masses of lower crust.

Early to Middle Tertiary intermediate to silicic composition volcanic rocks, Eastern Nevada

Dominantly intermediate to silicic composition, early to middle Tertiary volcanic rocks exposed in eastern Nevada are part of widespread, calc-alkaline volcanism that was associated with large magnitude extension (Gans and Miller, 1983; Gans et al., 1989). Based on work in eastern Nevada and western Utah, Gans et al. (1989) and Feeley and Grunder (1991) identified three stratigraphic and lithologic groups of rocks: early, middle and late. The early group, which is the most compositionally diverse, varies from basaltic andesite to rhyolite. For basaltic andesite to rhyodacite early group rocks, Grunder (1992) identified 3 distinct subsets: (1) fine-grained basaltic andesites to andesites that have few or no plagioclase phenocrysts; (2) basaltic andesites to rhyodacites that have disequilibrium textures indicative of magma mixing; and (3) andesites and dacites that have abundant plagioclase. Dacite to rhyolites of the middle group are hornblende-biotite bearing lavas that show disequilibrium textures similar to those identified in

the early group or textures that suggest they have achieved equilibrium. In general, compositional trends of middle group rocks are similar to the trends of early group rocks that exhibit evidence of magma mixing. Compositions of late group rocks are similar to those of middle group rocks, but are mainly biotite-bearing, crystal-poor, and exhibit equilibrium textures. In general, compared to early group rocks, middle and late group rocks are characterized by more radiogenic Sr isotopes, less radiogenic Nd isotopes, and exhibit less isotopic diversity.

To explain the isotopic and chemical diversity and the complex textures of the early group, Grunder (1992) proposes a 2-stage AFC process. The fine-grained mafic rocks exhibit increasing [Sr] with increasing $^{87}\text{Sr}/^{86}\text{Sr}$ and increasing [Nd] with decreasing $^{143}\text{Nd}/^{144}\text{Nd}$ (Fig. 15a, b), characteristics that are consistent with AFC. 'Classical' AFC modeling suggests involvement of large masses of assimilated ($r = 0.8$) that is rich in Nd but poor in Sr (AFC₁, Grunder, 1992). Based on the relatively low Sr concentrations in the assimilated, Grunder (1992) suggests that plagioclase is residual during partial melting of country rock. Sr is modeled to behave relatively incompatibly during fractional crystallization, consistent with observation that plagioclase is in limited abundance in the fine-grained mafic samples. Grunder concludes that the fine-grained mafic rocks derive by assimilation of 25-35% partial melt of early Proterozoic crust of pelitic composition. The compositions and textures of the mixed group suggest they derive by simple mixing of AFC₁-type assimilated and a slightly (10%) differentiated mafic magma. Compared to the fine-grained mafic samples, the plagioclase-rich samples of the early group have similar or lower Nd at lower $^{143}\text{Nd}/^{144}\text{Nd}$. Compared to other samples in the early group with similar $^{143}\text{Nd}/^{144}\text{Nd}$, the plagioclase-rich samples have relatively high $^{87}\text{Sr}/^{86}\text{Sr}$. Because of the abundance of plagioclase in these rocks, Sr is modeled as a compatible element during fractional

crystallization. Their compositions require assimilation of a contaminant that is rich in Sr but poor in Nd (AFC₂), and Grunder (1992) suggests that the magmas derive by AFC of large masses of crust ($r = 0.9$), where the assimilant is most likely the residue of partial melting associated with the AFC₁ 'event'.

Middle group samples that have textures suggestive of magma mixing originate by the same mechanism as mixed samples in the early group. The remaining middle and all late group samples exhibit little isotopic diversity, and Grunder suggests that magmas associated with these groups experienced minimal assimilation ($r = 0.2-0.3$) during fractional crystallization.

The 2-stage model proposed by Grunder is significant in that it recognizes the critical importance that country rock partial melting plays in AFC. Although rarely modeled, changes in elemental concentrations of country rock as it partially melts are critical to realistic AFC models. As Grunder recognized, a single 'classical' AFC model can not account for the increasing, then decreasing [Sr] at more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ nor the increasing, then decreasing [Nd] at less radiogenic $^{143}\text{Nd}/^{144}\text{Nd}$. EC-AFC model parameters (Table 4) were chosen, where possible, to be similar to those proposed by Grunder. Specifically, the degree of melting of pelite was chosen to be ~50%, consistent with the range estimated by Grunder (10-50%), and the behavior of Sr during fractional crystallization changed from incompatible to compatible during crystal fractionation. In addition, most of the compositional parameters are similar. The EC-AFC results describe well the range of Sr- $^{87}\text{Sr}/^{86}\text{Sr}$ and Nd- $^{143}\text{Nd}/^{144}\text{Nd}$ for most samples (Fig. 15a, b, c). A degree of compositional heterogeneity is required for both parental magmas and country rock (Table 4), consistent with the complex history of the associated crust and magma source(s). Several points regarding the EC-AFC results are significant. The fine-grained mafic samples and plagioclase-rich samples are explained by assimilation of crust that undergoes continuous

fractional melting, a scenario that is probably more physically plausible than assimilation in two discrete stages. In order to explain some of the Nd-poor rhyolites, country rock Nd must be modeled to increase its incompatibility during partial melting; by invoking a strong temperature dependence (Table 4), D_{Nd} of the assimilant during partial melting ranges from 0.16 to ~ 0.01 . Such incompatible behavior strips the country rock of Nd, thereby decreasing its abundance in the contaminated magma (by dilution) while maintaining relatively constant $^{143}Nd/^{144}Nd$. Such low bulk distribution coefficients suggest that a REE-bearing phase may have preferentially melted and was largely eliminated from the country rock residue during the AFC process. This possibility can be evaluated by investigating the behavior of other REE. Another possibility is that Nd became compatible during fractional crystallization, although Grunder (1992) models the element as incompatible during fractional crystallization. The incompatible behavior of Sr in the country rock coupled with its early behavior as incompatible during fractional crystallization can explain the positive $[Sr]^{-87}Sr/^{86}Sr$ correlation among the fine-grained mafic rocks. In the EC-AFC models, Sr in the magma body is modeled to have a strong temperature dependence (Table 4), which allows the bulk distribution coefficient to vary smoothly from ~ 0.6 to 1.4 during fractional crystallization and accommodates the observed changes in plagioclase abundance. Thus, depletion of Sr from country rock residue coupled with the element's increasingly compatible behavior accounts for the decrease in $[Sr]$ at relatively constant $^{87}Sr/^{86}Sr$ (~ 0.7120 to 0.7140). The more radiogenic Sr isotope signatures of the plagioclase-rich rocks, compared to other early group samples, are also well modeled by the EC-AFC results (Fig. 15c, E. NV 3 trend).

Compositions of the middle and late group rocks are explained by the same EC-AFC models as those of the early group. Because of their low degree of isotopic variability, Grunder suggests

that the associated magmas were dominated by fractional crystallization and experienced low rates of assimilation. For AFC trends modeled using the ‘classical’ solutions, such an explanation is the only possible one because ‘classical’ AFC trends do not flatten out. However, such trends are a characteristic of EC-AFC models in which elements in the country rock behave incompatibly. Rather than reflecting lower rates of assimilation, the associated magmas have assimilated the largest mass of anatectic melt.

Summary

For the Long Valley and CRB suites, our interpretations of the EC-AFC results suggest assimilation involved country rock more mafic than proposed by previous workers. In the case of the eastern Nevada samples, EC-AFC largely confirms the model of Grunder (1992) but provides a more plausible physical framework for the process. In all cases, geochemically and geologically relevant predictions are made by the EC-AFC results; pursuing these predictions will enhance our understanding of these magmatic systems as well open-system processes in general.

The three cases discussed in this section were chosen to demonstrate distinctions between EC-AFC and ‘classical’ AFC models and to also provide a clear demonstration of the improvements offered by EC-AFC. These include the ability to incorporate compositional variations of country rock partial melts into the chemical evolution of the magma body and the ability to link the thermal and compositional evolution of the composite magma body-country rock system. We suggest that even when ‘classical’ AFC and EC-AFC results are similar, EC-AFC is a superior modeling tool because it couples thermal and chemical parameters, which, in turn, offers the prospect of developing more realistic open-system magma chamber models.

CONCLUSIONS

EC-AFC is a new formulation of AFC that conserves energy, species and mass while also incorporating the compositional variations generated in anatectic melt as country rock undergoes partial fusion. A critical aspect of the formulation is that it links thermochemical and thermophysical parameters of an open-system magma body. The geochemical consequences EC-AFC are significant. Compared to 'classical' AFC models that conserve mass and species only, EC-AFC geochemical trends are distinct, exhibiting non-monotonic behaviors that are linked to energy conservation and country rock partial melting. We show that particular conclusions about some compositional trends associated with 'classical' AFC are not necessarily correct. Among these are the observations that trends such as $1/\text{Sr}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ need not be monotonic for AFC to be important, that there is not necessarily a positive correlation between degree of differentiation (e.g., as measured by abundances of incompatible trace elements) and extent of contamination (as measured by mass of anatectic melt assimilated), and that the magma body that has assimilated the largest mass of anatectic melt may not necessarily exhibit an isotope signature most like that of the wallrock. Another critical outcome is that reasonable EC-AFC input parameters show that relatively radiogenic Sr isotope signatures can be achieved with addition of small masses of assimilant; this has implications for the origin of isotopically 'enriched' basalts. Comparison between results of 'classical' AFC and EC-AFC for data from a variety of volcanic centers demonstrates that EC-AFC does a superior job of modeling the compositional trends, provides a plausible physical context for the process of AFC, and allows geologically relevant predictions to be made about magmatic systems. We anticipate that results

of EC-AFC models will lead to significant new discoveries regarding the nature of open-system magma systems.

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FIGURE CAPTIONS

Fig. 1a: Melt temperature (T_m) *versus* restite temperature (T_a) and mass of melt in magma body (M_m); **Fig 1b:** T_m *versus* mass of anatectic melt added to the magma body (M_a^*) and mass of cumulates formed (M_c); **Fig. 1c:** T_m *versus* M_a^*/M_c for three simulations over the temperature interval T_m^0 to T_{eq} : ‘standard’ upper crustal case (circles), ‘nonlinear’ upper crustal case (diamonds), and ‘standard’ lower crustal case (squares). For Fig. 1a and 1b, filled symbols are T_a ($^{\circ}\text{C}$) and M_a^* whereas open symbols are M_m and M_c . Each symbol represents a normalized temperature increment of 0.02 ($\sim 30^{\circ}\text{C}$ decrease in T_m for all cases). See Table 1 for thermal input parameters.

Fig. 2: Melt productivity (fraction of melt-temperature relations) for magma body (f_m) and country rock (f_a) for ‘nonlinear’ upper crustal case. Note that the X-axis is the magma body temperature.

Fig. 3a: Comparison of Sr (ppm) *versus* $^{87}\text{Sr}/^{86}\text{Sr}$ results for EC-AFC models of ‘standard’ (filled circles) and ‘nonlinear’ (diamonds) upper crustal and ‘standard’ (filled squares) lower crustal cases and ‘classical’ upper (open circles) and lower (open squares) crustal cases. EC-AFC parameters in Table 1. For EC-AFC trends, arrows illustrate direction of decreasing T_m , and each symbol represents a normalized temperature increment of 0.02 ($\sim 30^{\circ}\text{C}$ decrease in T_m for all cases). For ‘classical’ AFC trends, symbols represent a fraction of melt (F) increment of 0.1 but are terminated at $F = 0.05$. Where appropriate, parameters for ‘classical’ AFC trends are the same as those of EC-AFC. For the upper crustal case, $r = 0.33$ and for the lower crustal case, $r = 0.17$, which are average M_a^*/M_c . **Fig. 3b:** Concentration of Sr in anatectic melt generated from

country rock undergoing fractional melting, where Sr behaves incompatibly ($D_a = 0.05$; 'standard' lower crustal case), and Sr_a^0 is 230 ppm. Sr concentration shown for $f_a(T_a)$ up to 1.00. For 'standard' lower crustal case, $f_a(T_a)$ at T_{eq} is 0.21.

Fig. 4a: Comparison of Sr (ppm) *versus* $^{87}Sr/^{86}Sr$ results for EC-AFC and 'classical' AFC models of upper crustal contamination, where Sr_a^0 varies. Arrows same as Fig. 3a. **Fig. 4b:** Concentration of Sr in anatectic melt generated from country rock undergoing fractional melting, where Sr behaves compatibly ($D_a = 1.5$) and Sr_a^0 varies. Sr concentration shown for $f_a(T_a)$ up to 0.95. For 'standard' upper crustal case, $f_a(T_a)$ at T_{eq} is 0.86.

Fig. 5: Comparison of Nd (ppm) *versus* $^{143}Nd/^{144}Nd$ results for EC-AFC models of 'standard' and 'nonlinear' upper crustal and 'standard' lower crustal cases and 'classical' upper and lower crustal cases. Symbols and arrows same as Fig. 3a.

Fig. 6a: Comparison of Nd (ppm) *versus* Sr (ppm) results for EC-AFC and 'classical' AFC models of upper crustal and lower crustal contamination. Symbols and arrows same as Fig. 3a.

Fig. 6b: Comparison of Nd (ppm) *versus* Th (ppm) results for EC-AFC and 'classical' AFC models of upper crustal and lower crustal contamination. At the scale shown, the EC-AFC, lower trend increases and decreases in [Nd] and [Th] along a similar trajectory. For this case, the magma that has assimilated the largest mass of anatectic melt has ~83 ppm Nd and ~14 ppm Th. Symbols and arrows same as Fig. 3a.

Fig. 7a: Comparison of M_a^*/M_o versus Sr (ppm) results; **Fig. 7b:** M_a^*/M_o versus $^{87}\text{Sr}/^{86}\text{Sr}$ results for EC-AFC models of ‘standard’ upper crustal and lower crustal cases. Symbols and arrows same as Fig. 3a.

Fig. 8a: Comparison of M_a^*/M_o versus Sr (ppm) results for EC-AFC models of ‘standard’ upper crustal contamination where the initial concentration of Sr in the country rock, Sr_a^o , varies. Concentrations were chosen to reflect $\text{Sr}_m^o/\text{Sr}_a^o$ of 2/1 (upper), 3/1 (233 ppm), 4/1 (175 ppm). Sr_m^o is constant at 700 ppm. **Fig. 8b:** Comparison of M_a^*/M_o versus $^{87}\text{Sr}/^{86}\text{Sr}$ results for EC-AFC models of ‘standard’ upper crustal contamination. Different trends reflect variations in $\text{Sr}_m^o/\text{Sr}_a^o$. Sr isotope ratios of magma and country rock are constant at 0.7035 and 0.7220, respectively. **Fig. 8c:** Comparison of M_a^*/M_o versus Sr (ppm) results for EC-AFC models of ‘standard’ lower crustal contamination where Sr_a^o varies. Concentrations were chosen to reflect $\text{Sr}_m^o/\text{Sr}_a^o$ of 2/1 (350 ppm), 3/1 (lower), 4/1 (175 ppm). Sr_m^o is constant at 700 ppm. **Fig. 8d:** Comparison of M_a^*/M_o versus $^{87}\text{Sr}/^{86}\text{Sr}$ results for EC-AFC models of ‘standard’ lower crustal contamination. Different trends reflect variations in $\text{Sr}_m^o/\text{Sr}_a^o$. Sr isotope ratios of magma and country rock are constant at 0.7035 and 0.7100, respectively. Symbols and arrows same as Fig. 3a.

Fig. 9a: Comparison of M_a^*/M_o versus Sr (ppm) results; **Fig. 9b:** M_a^*/M_o versus $^{87}\text{Sr}/^{86}\text{Sr}$ results; **Fig. 9c:** M_a^*/M_o versus Nd (ppm) results; **Fig. 9d:** M_a^*/M_o versus $^{143}\text{Nd}/^{144}\text{Nd}$ results for EC-AFC models of ‘standard’ upper crustal case, where T_{eq} varies. Symbols and arrows same as Fig. 3a.

Fig. 10a: Comparison of M_a^*/M_o versus $^{87}\text{Sr}/^{86}\text{Sr}$ results; **Fig. 10b:** M_a^*/M_o versus $^{143}\text{Nd}/^{144}\text{Nd}$ results for EC-AFC models of ‘standard’ upper crustal case, where $T_{l,a}$ and $T_{l,m}$ - T_m^o vary. Symbols and arrows same as Fig. 3a.

Fig. 11a: Comparison of Sr (ppm) versus $^{87}\text{Sr}/^{86}\text{Sr}$ results; **Fig. 11b:** Nd (ppm) versus $^{143}\text{Nd}/^{144}\text{Nd}$ results for EC-AFC models of ‘standard’ upper crustal case, where T_s varies. Symbols and arrows same as Fig. 3a.

Fig. 12a: Comparison of Sr (ppm) versus $^{87}\text{Sr}/^{86}\text{Sr}$ results; **Fig. 12b:** Nd (ppm) versus $^{143}\text{Nd}/^{144}\text{Nd}$ results for EC-AFC models of ‘standard’ upper crustal case where T_a^o varies. Symbols and arrows same as Fig. 3a.

Fig. 13: Sr versus $^{87}\text{Sr}/^{86}\text{Sr}$ data (filled gray circles) and results of EC-AFC and ‘classical’ AFC simulations for mafic-intermediate volcanic rocks from the Long Valley caldera and Devil’s Postpile National Monument, eastern, CA (Vogel et al., 1994; Cousens, 1996). EC-AFC parameters in Table 2. Arrows illustrate direction of decreasing T_m , and each symbol represents a normalized temperature increment of 0.02 (~30° C decrease in T_m). ‘Classical’ AFC parameters: upper- $\text{Sr}_m^o = 800$ ppm, $\text{Sr}_a^o = 250$ ppm, $^{87}\text{Sr}/^{86}\text{Sr}_m^o = 0.70596$, $^{87}\text{Sr}/^{86}\text{Sr}_a^o = 0.70660$, $D_{\text{Sr}} = 1.5$, $r = 0.2$; lower- $\text{Sr}_m^o = 800$ ppm, $\text{Sr}_a^o = 250$ ppm, $^{87}\text{Sr}/^{86}\text{Sr}_m^o = 0.70596$, $^{87}\text{Sr}/^{86}\text{Sr}_a^o = 0.70660$, $D_{\text{Sr}} = 0.33$, $r = 0.8$. For ‘classical’ AFC trends, symbols represent a fraction of melt (F) increment of 0.1 but are terminated at $F = 0.05$.

Fig. 14: Sr versus $^{87}\text{Sr}/^{86}\text{Sr}$ data (Grande Ronde basalts, filled circles; Imnaha basalts, filled squares; Carlson et al., 1981; Hooper and Hawkesworth, 1992) and results of EC-AFC and ‘classical’ AFC simulations for Columbia River Basalts. EC-AFC parameters for CRB1, CRB2, and CRB3 in Table 3. Arrows illustrate direction of decreasing T_m , and each symbol represents a normalized temperature increment of 0.02 ($\sim 30^\circ\text{C}$ decrease in T_m). ‘Classical’ AFC parameters are similar to those of Carlson et al., (1981): $\text{AFC}_1\text{-Sr}_m^o = 250\text{ ppm}$, $\text{Sr}_a^o = 50\text{ ppm}$, $^{87}\text{Sr}/^{86}\text{Sr}_m^o = 0.7035$, $^{87}\text{Sr}/^{86}\text{Sr}_a^o = 0.7600$, $D_{\text{Sr}} = 0.2$, $r = 0.25$; $\text{AFC}_2\text{-Sr}_m^o = 400\text{ ppm}$, $\text{Sr}_a^o = 50\text{ ppm}$, $^{87}\text{Sr}/^{86}\text{Sr}_m^o = 0.7035$, $^{87}\text{Sr}/^{86}\text{Sr}_a^o = 0.723$, $D_{\text{Sr}} = 1$, $r = 0.25$. For ‘classical’ AFC trends, symbols represent a fraction of melt (F) increment of 0.1.

Fig. 15a: Sr versus $^{87}\text{Sr}/^{86}\text{Sr}$ data (filled gray circles) and results of EC-AFC and ‘classical’ AFC simulations for dominantly intermediate composition volcanic rocks from eastern Nevada (Grunder, 1992). EC-AFC parameters for E. NV 1, E. NV 2, and E. NV 3 in Table 4. Arrows illustrate direction of decreasing T_m , and each symbol represents a normalized temperature increment of 0.02 ($\sim 30^\circ\text{C}$ decrease in T_m). ‘Classical’ AFC parameters are those of Grunder (1992): $\text{AFC}_1\text{-Sr}_m^o = 450\text{ ppm}$, $\text{Sr}_a^o = 350\text{ ppm}$, $^{87}\text{Sr}/^{86}\text{Sr}_m^o = 0.7080$, $^{87}\text{Sr}/^{86}\text{Sr}_a^o = 0.7150$, $D_{\text{Sr}} = 0.4$, $r = 0.8$; $\text{AFC}_2\text{-Sr}_m^o = 640\text{ ppm}$, $\text{Sr}_a^o = 700\text{ ppm}$, $^{87}\text{Sr}/^{86}\text{Sr}_m^o = 0.7111$, $^{87}\text{Sr}/^{86}\text{Sr}_a^o = 0.7150$, $D_{\text{Sr}} = 1.5$, $r = 0.9$. For ‘classical’ AFC trends, symbols represent a fraction of melt (F) increment of 0.1. **Fig. 15b:** Nd versus $^{143}\text{Nd}/^{144}\text{Nd}$ data (filled gray circles) and results of EC-AFC and ‘classical’ AFC simulations. ‘Classical’ AFC parameters are those of Grunder (1992): $\text{AFC}_1\text{-Nd}_m^o = 20\text{ ppm}$, $\text{Nd}_a^o = 45\text{ ppm}$, $^{143}\text{Nd}/^{144}\text{Nd}_m^o = 0.51245$, $^{143}\text{Nd}/^{144}\text{Nd}_a^o = 0.51161$, $D_{\text{Nd}} = 0.4$, $r = 0.8$; $\text{AFC}_2\text{-Nd}_m^o = 52\text{ ppm}$, $\text{Nd}_a^o = 5\text{ ppm}$, $^{143}\text{Nd}/^{144}\text{Nd}_m^o = 0.51187$, $^{143}\text{Nd}/^{144}\text{Nd}_a^o =$

$=0.51161$, $D_{\text{Nd}} = 0.6$, $r = 0.9$. **Fig. 15c:** $^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$ data (filled gray circles) and results of EC-AFC and 'classical' AFC simulations.

Table 1a: EC-AFC Parameters for ‘Standard’ Upper Crustal Case and ‘Nonlinear’ Upper Crustal Case

Thermal Parameters			
magma liquidus temperature, $T_{l,m}$	1280°C	crystallization enthalpy, h_{cry} (J/kg)	396000
magma initial temperature, T_m^o	1280°C	isobaric specific heat of magma, $C_{p,m}$ (J/kgK)	1484
assimilant liquidus temperature, $T_{l,a}$	1000°C	fusion enthalpy, h_{fus} (J/kg)	270000
assimilant initial temperature, T_a^o	300°C	isobaric specific heat of assimilant, $C_{p,a}$ (J/kgK)	1370
solidus temperature, T_s	900°C		
equilibration temperature, T_{eq}	980°C		

Compositional Parameters

	Sr	Nd	Th
magma initial conc. (ppm), C_m^o	700	35	5
magma isotope ratio, α_m	0.7035	0.5130	-
magma trace element distribution coefficient, D_m	1.5	0.25	0.1
enthalpy of trace element distribution reaction, H_m	-	-	-
assimilant initial conc. (ppm), C_a^o	350	26	10.7
assimilant isotope ratio, α_a	0.7220	0.5118	-
assimilant trace element distribution coefficient, D_a	1.5	0.25	0.1
enthalpy of trace element distribution reaction, H_a	-	-	-

Table 1b: EC-AFC Parameters for ‘Standard’ Lower Crustal Case

Thermal Parameters			
magma liquidus temperature, $T_{l,m}$	1320°C	crystallization enthalpy, h_{cry} (J/kg)	396000
magma initial temperature, T_m^o	1320°C	isobaric specific heat of magma, $C_{p,m}$ (J/kgK)	1484
assimilant liquidus temperature, $T_{l,a}$	1100°C	fusion enthalpy, h_{fus} (J/kg)	354000
assimilant initial temperature, T_a^o	600°C	isobaric specific heat of assimilant, $C_{p,a}$ (J/kgK)	1388
solidus temperature, T_s	950°C		
equilibration temperature, T_{eq}	980°C		

Compositional Parameters			
	Sr	Nd	Th
magma initial conc. (ppm), C_m^o	700	25	5
magma isotope ratio, r_m	0.7035	0.5130	-
magma trace element distribution coefficient, D_m	1.5	0.25	0.1
enthalpy of trace element distribution reaction, H_m	-	-	-
assimilant initial conc. (ppm), C_a^o	230	12.7	1.06
assimilant isotope ratio, r_a	0.7100	0.5122	-
assimilant trace element distribution coefficient, D_a	0.05	0.25	0.1
enthalpy of trace element distribution reaction, H_a	-	-	-

Table 2: EC-AFC Parameters, Mafic Volcanic Rocks from near Long Valley, CA.

Thermal Parameters			
magma liquidus temperature, $T_{l,m}$	1200°C	crystallization enthalpy, h_{cry} (J/kg)	350000
magma initial temperature, T_m^o	1200°C	isobaric specific heat of magma, $C_{p,m}$ (J/kgK)	1300
assimilant liquidus temperature, $T_{l,a}$	1100°C	fusion enthalpy, h_{fus} (J/kg)	250000
assimilant initial temperature, T_a^o	550°C	isobaric specific heat of assimilant, $C_{p,a}$ (J/kgK)	1300
solidus temperature, T_s	800°C		
equilibration temperature, T_{eq}	850°C		
Compositional Parameters			
		Sr	
magma initial conc. (ppm), C_m^o	1150		
magma isotope ratio, r_m	0.70596		
magma trace element distribution coefficient, D_m	1.5		
enthalpy of trace element distribution reaction, H_m	-		
assimilant initial conc. (ppm), C_a^o	200		
assimilant isotope ratio, r_a	0.70655		
assimilant trace element distribution coefficient, D_a	0.025		
enthalpy of trace element distribution reaction, H_a	-		

Table 3: EC-AFC Parameters, Columbia River Basalt

Thermal Parameters			
magma liquidus temperature, $T_{l,m}$	1300°C	crystallization enthalpy, h_{cry} (J/kg)	396000
magma initial temperature, T_m^o	1300°C	isobaric specific heat of magma, $C_{p,m}$ (J/kgK)	1484
assimilant liquidus temperature, $T_{l,a}$	1150°C	fusion enthalpy, h_{fus} (J/kg)	270000
assimilant initial temperature, T_a^o	600°C	isobaric specific heat of assimilant, $C_{p,a}$ (J/kgK)	1370
solidus temperature, T_s	900°C		
equilibration temperature, T_{eq}	1100°C		

Compositional Parameters			
	CRB 1	CRB 2	CRB 3
magma initial conc. (ppm), C_m^o	400	375	325
magma isotope ratio, r_m	0.70388	0.70388	0.70388
magma trace element distribution coefficient, D_m	1 (1.5-17)*	1 (1.7-1.8)*	1.3 (2.2-2.4)*
enthalpy of trace element distribution reaction, H_m	-6000	-7000	-7000
assimilant initial conc. (ppm), C_a^o	150	125	220
assimilant isotope ratio, r_a	0.709	0.712	0.708
assimilant trace element distribution coefficient, D_a	0.05	0.05	0.05
enthalpy of trace element distribution reaction, H_a	-	-	-

* reported value of D is that input into EC-AFC computer program; values in parentheses are effective range when temperature dependence of D is explicitly accounted for (see Appendix I, Spera and Bohrsen, 2000, this volume).

Table 4: EC-AFC Parameters, Intermediate Rocks, Eastern Nevada

Thermal Parameters						
magma liquidus temperature, $T_{l,m}$	1200°C	crystallization enthalpy, h_{cry} (J/kg)	396000			
magma initial temperature, T_m^o	1200°C	isobaric specific heat of magma, $C_{p,m}$ (J/kgK)	1484			
assimilant liquidus temperature, $T_{l,a}$	850°C	fusion enthalpy, h_{fus} (J/kg)	270000			
assimilant initial temperature, T_a^o	500°C	isobaric specific heat of assimilant, $C_{p,a}$ (J/kgK)	1370			
solidus temperature, T_s	800°C					
equilibration temperature, T_{eq}	825°C					
Compositional Parameters						
	E. NV 1 Sr	E. NV 1 Nd	E. NV 2 Sr	E. NV 2 Nd	E. NV 3 Sr	E. NV 3 Nd
magma initial conc. (ppm), C_m^o	375	14	375	8	375	12
magma isotope ratio, m	0.708	0.5123	0.708	0.5123	0.708	0.5123
magma trace element distribution coefficient, D_m	0.048 (0.6-1.4)*	0.3	0.048 (0.6-1.4)*	0.3	0.048 (0.6-1.4)*	0.3
enthalpy of trace element distribution reaction, H_m	-31000	-	-31000	-	-31000	-
assimilant initial conc. (ppm), C_a^o	180	20	195	15	225	15
assimilant isotope ratio, a	0.715	0.51135	0.716	0.5115	0.717	0.5115
assimilant trace element distribution coefficient, D_a	0.05	0.0025 (0.07-0.26)*	0.05	0.006 (0.05-0.14)*	0.05	0.00003 (0.01-0.16)*
enthalpy of trace element distribution reaction, H_a	-	-30000	-	-20000	-	-55000

* reported value of D is that input into EC-AFC computer program; values in parentheses are effective range when temperature dependence of D is explicitly accounted for (see Appendix I, Spera and Bohrsen, 2000, this volume).