

**Energy-Constrained Open-System Magmatic Processes I:  
General Model and Energy-Constrained Assimilation and  
Fractional Crystallization (EC-AFC) Formulation**

Frank J. Spera<sup>1</sup> and Wendy A. Bohron<sup>2</sup>

Institute for Crustal Studies and Department of Geological Sciences, University of  
California, Santa Barbara, CA. USA 93106

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<sup>1</sup> Corresponding author: Tele (805) 893- 4880; Fax (805) 893-2314, email [spera@magma.geol.ucsb.edu](mailto:spera@magma.geol.ucsb.edu)

<sup>2</sup> Now at: Department of Geological Sciences, Central Washington University, Ellensburg, WA. USA 98926

## ABSTRACT

Geochemical data for igneous rocks provide definitive evidence for the occurrence of open-system processes in magma bodies, including **R**eplenishment by intrusion of primitive magma, **A**ssimilation of anatectic wallrock melt and cumulate formation by **F**ractional **C**rystallization. A general class of models (**E**nergy **C**onserved-RAFC or EC-RAFC) can be constructed which enable simulation of geochemical paths for trace elements and isotopic ratios for magma undergoing simultaneous replenishment, assimilation and fractional crystallization during the approach to thermal equilibration. The general problem of EC-RAFC is formulated as a set of  $3+t+i+s$  coupled nonlinear ordinary differential equations, where the number of trace elements, radiogenic and stable isotope ratios simultaneously modeled are  $t$ ,  $i$  and  $s$ , respectively. Partial melting of wallrock, modeled as fractional melting, is incorporated, as are sensible and latent heat effects. Temperature-dependent partition coefficients are used to describe trace element distributions. Solution of the set of differential equations, with magma temperature ( $T_m$ ) as the independent variable, provides values for the average temperature of wallrock ( $T_a$ ), fraction of melt within the magma body ( $M_m$ ), mass of cumulates ( $M_c$ ) formed, mass of wall rock involved in the thermal interaction ( $M_a^0$ ), mass of anatectic melt assimilated ( $M_a^*$ ), the concentration of  $t$  trace elements ( $C_m$ ) and  $i+s$  isotopic ratios ( $\epsilon_m$ ) in magma (melt plus cumulates) and in anatectic melt delivered to the evolving magma body. Input parameters include a user-defined equilibration temperature ( $T_{eq}$ ), the initial temperatures and compositions of magma, recharge magma, and wallrock, distribution coefficients and their temperature dependencies, heats of fusion and crystallization and isobaric specific heat capacities of the various constituents. *For a priori*

defined magma recharge mass and  $T_{eq}$ , the mass of wallrock heated to  $T_{eq}$  is computed and the geochemical trajectory of melt is determined as magma temperature approaches  $T_{eq}$  from its starting value,  $T_m^0$ . The effects of imperfect extraction of anatectic wallrock melt may be accounted for by introduction of an extraction efficiency factor. Mathematical details of a simpler model, EC-AFC (no replenishment) are provided. Energy constrained models have the advantage of linking thermal and chemical properties of magma chambers. Compared to 'classical' models that conserve mass and species only, they represent more complete assessments of the complex physiochemical dynamics governing the geochemical evolution of open-system magma bodies. Results of EC-AFC simulations demonstrate that geochemical trends can differ significantly from predictions based on 'classical' AFC even when recharge plays no role. Incorporation of energy conservation and partial melting into geochemical models allows important coupled effects to play their natural role.

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

## INTRODUCTION

Magmatism represents an important mechanism for transport of energy and matter within the mantle and between the mantle and crust on the terrestrial planets. On Earth, roughly  $30 \text{ km}^3$  of magma is generated and emplaced into or onto the crust each year (Shaw, 1973; Crisp, 1984). By this reckoning, a volume of mafic magma equal to 15 percent of the mantle has been extracted since the beginning of the Archean 4.0 Gyr ago. When allowance is made for magma generation during the Hadean, an inescapable conclusion is that a significant fraction, perhaps exceeding half, of the mantle has undergone at least one cycle of partial melting. The transport of material and heat by magmatic processes has played an important if not defining role in the geological (tectonic and geochemical) evolution of Earth.

Magma acts as an efficient heat-transfer agent. Advection of heat is geologically rapid (e.g., Spera, 1984) and proportional to the amount and rate of magma transport as well as to its calorimetric properties. On a longer timescale, the redistribution of incompatible radiogenic elements (K, U and Th) during partial melting, a process controlled by atomic scale crystal/melt cation exchange reactions, also contributes to heat transfer and the geotherm.

Melts generated in the mantle are the dominant contributors to the formation of continental crust by accretion of subduction-derived arc terranes (e.g., Ernst, 1999) or mafic oceanic plateaus onto pre-existing cratons. Intrusion of mafic magmas beneath, into or onto pre-existing crust (mafic plating) may be an equally important mechanism for crustal growth. The processes of anatexis (partial melting of pre-existing crystalline rock) and fractional crystallization typically leave geochemical fingerprints in an evolving magma body, betraying both chemical and thermal interaction with surroundings. This is especially apparent when magma and host are

compositionally and thermodynamically distinct. An aim of modern geochemistry is to interpret these fingerprints in light of petrologic processes and thereby constrain the geologic history of a magma body. This history can then be fitted into the larger tectonic context and afford better comprehension of the thermal and chemical evolution of Earth.

Although many facets of the compositional diversity problem have been studied, indeed this issue lies at the very heart of igneous petrology, there is no *general* formulation for open magmatic systems that self-consistently treats energy, momentum and material conservation during country rock partial melting, magma replenishment and intra-chamber cumulate formation. There are several classes of extant models. Thermodynamically-based transport models (e.g., Spera et al., 1982; Sparks, 1986; Ghiorso and Kelemen, 1987; Huppert and Sparks, 1988; Marsh, 1989; Kelemen, 1990; Spera et al., 1995; Raia and Spera, 1997; Barboza and Bergantz, 1997, 1998; Marsh, 1998; Weinberg and Leitch, 1998) account for energy balance, phase equilibria and rheological effects but generally ignore isotopic and trace element constraints. In transport models where geochemical details are explicitly considered, the physical model is often very specific in terms of process or configuration. Generality is sometimes compromised for the sake of tractability. It is often difficult to recognize when the model applies to real systems. On the other hand, 'classical' replenishment, assimilation and fractional crystallization geochemical models (e.g., DePaolo, 1981; O'Hara, 1995, 1998), while characterizing the geochemical evolution of a magma in detail, neglect important constraints imposed by energy conservation, the thermodynamics of partial melting, and the dynamics of melt extraction and magma mixing.

In the model developed here and applied to a number of systems in Bohrson and Spera (2000, this volume), we attempt to bridge the gap between these approaches by combining constraints

from energy conservation in partially molten systems with material balance relations for trace elements and isotopic ratios. The general model also incorporates constraints from momentum conservation in an approximate way. The model is zero dimensional in the sense that spatial fields are not explicitly considered. The parameterization involves energy, mass, and isotopic and trace element conservation applied to arbitrary-sized open magmatic systems undergoing concurrent magma replenishment, assimilation of anatectic melts and formation of cumulates by fractional crystallization. The main purpose is to develop and make available to the petrologic community an energy-constrained model for the evolution of trace elements and isotopic ratios in a magma body. Ease of application to natural systems is an important objective. There are thousands of magmatic systems that have been compositionally characterized. A purpose of this study is to provide a general tool, easily applied to such systems, to gain further geological insight.

### **ENERGY-CONSTRAINED OPEN-SYSTEM MAGMATIC PROCESSES: SYNOPSIS**

Natural systems can be modeled as energy-conserving open composite systems sealed off adiabatically from the rest of their surroundings. The assumption of adiabaticity implies a regional length scale; obviously, it is only at such scales that the adiabatic approximation is valid. Adiabaticity facilitates the analysis of EC-RAFC processes and allows for application to a wide variety of natural systems. The sub-systems making up the composite system include country rock, magma body, and a reservoir of recharge magma that are separated from one another by diathermal and open (permeable) boundaries that allow complete or partial heat and species exchange. The sub-systems themselves can be viewed as composite systems so that

compositionally zoned magma bodies can be treated. Within this hierarchical framework, the energy-constrained formulation presented here for a (homogeneous) magma body consists of a set of  $3+t+i+s$  coupled ordinary differential equations expressing conservation of energy (enthalpy), total mass,  $t$  trace element species and  $i+s$  isotopic ratios. The independent variable is conveniently taken as the temperature of melt ( $T_m$ ) within the magma sub-system, which is comprised of melt plus cumulates. Tracking the geochemical path during RAFC demands an accurate rendering of phase relations which govern trace element mineral/melt and fluid/melt distribution coefficients including variations with composition and temperature as well as the thermal properties and melt productivity functions for magma, crust and recharge magma. Results from both experimental phase equilibria and thermodynamic modeling (e.g., MELTS, Ghiorso, 1997) may be used to constrain the thermodynamics of melting, and these constraints can then be included explicitly into the general EC formulation thereby accounting for major element constraints. The energy-constrained formulation incorporates geological and geochemical information along with thermophysical and thermochemical parameters relevant to a specific magmatic system, thereby providing a holistic view of an evolving magma body. A schematic representation of EC-RAFC processes is pictured in Fig. 1.

Unfortunately, accurate accounting of momentum, chemical species and heat exchange during open-system processes demands precise knowledge of the size and configuration of the system in addition to a host other details unique to a particular system. Development of a general 3-dimensional thermodynamic and fluid dynamic model to account for the variability of natural systems is bewilderingly complex and not attempted here. We adopt the more limited goal of establishing a class of models that self-consistently accounts for mass, species and energy

conservation within a 'simple' composite system framework. Predictions of this model may then be compared with voluminous data from natural systems.

In this paper, the conceptual framework, assumptions and approximations of the general EC-RAFC model are first discussed. Following this, the more specific application, EC-AFC is presented in quantitative terms. Although recharge is undoubtedly an important process in many natural systems, it is useful to first consider the implications of energy conservation and partial melting to systems dominated by AFC processes. The full differential equations for EC-RAFC will be presented elsewhere. A computer program for performing EC-AFC computations is available at <http://magma.geol.ucsb.edu/research/recharge.html>. The program may also be obtained from the *Journal of Petrology* web site. In the companion paper (Bohrson and Spera, 2000, this volume), the geochemical implications of EC-AFC are discussed and the model is applied to a number of natural systems.

## **ENERGY-CONSTRAINED OPEN-SYSTEM MAGMATIC PROCESSES: CONCEPTUAL FRAMEWORK AND BACKGROUND**

### **Historical Perspective on Recharge, Assimilation, and Fractional Crystallization (RAFC)**

#### **Models**

Crustal assimilation and reaction of assimilated material with magma together with fractional crystallization have been recognized as important petrogenetic processes for over a century.

Studies on the Tertiary volcanic centers of western Scotland (Harker, 1904; Bailey et. al., 1924; Thomas, 1922; Tyrrell, 1928), from Hakone volcano, Japan (Kuno, 1950) and at Paricutin,



Mexico (Wilcox, 1954) emphasized the necessity of invoking assimilation of anatectic melts to explain petrographic observations and chemical trends. Early treatments relied mostly on phase equilibrium arguments. The classic treatment by Bowen (1922a, 1922b, and 1928) enumerates possible consequences of assimilation of igneous and sedimentary rocks based on phase equilibria and remains vital to this day. Kelemen (1990) reviews the assimilation-reaction concept with a special focus on isenthalpic constraints and accurate rendering of phase relations by minimization of appropriate thermodynamic potentials. He has argued that assimilation-reaction of peridotite by ascending olivine tholeiitic magmas combined with crystal fractionation can give rise to calc-alkaline and basaltic andesitic liquids so common in island arc environments.

Attention to the effects of assimilation on trace element and isotopic signatures helped usher in the modern era of study of assimilation. Investigations of Pb isotopes (e.g., Doe, 1967, Doe et al., 1968, Church, 1976) and Sr-Nd isotopes (Carter et al., 1978) underscored the importance of crustal contamination as a mechanism for imparting 'enriched' isotope signatures in continental volcanic and plutonic suites. Noting the existence of magmatic systems characterized by radiogenic Sr and  $^{18}\text{O}$  enrichments, Taylor and colleagues (Taylor et al., 1979; Taylor, 1980), James (1981) and others (e.g., Hoefs et al., 1980) documented cases where assimilation was clearly at work (e.g., Roccamonfina). The pairing of Sr and O isotopes is especially telling because processes that lead to enrichments in each can be very different. Radiogenic Sr comes from decay of high Rb/Sr sources, typically of continental origin, whereas elevated  $^{18}\text{O}$  is commonly the result of low-temperature interaction between rock and fluid, a common upper crustal process. Thus, identification of high  $^{87}\text{Sr}/^{86}\text{Sr}$ - $^{18}\text{O}/^{16}\text{O}$  rocks led these authors to recognize

the contribution that crust and crustal fluids have in the isotopic and trace element characteristics of many igneous suites.

The process of crustal assimilation was initially viewed as a two-component problem involving mixing between magma and wallrock melt. Taylor and colleagues (Taylor et al., 1979; Taylor, 1980) underscored the point made by Bowen, that assimilation of crustal material was inextricably linked to the process of fractional crystallization. The lack of superheated magmas implies that an important source of heat for melting wallrock is the latent heat of crystallization (cumulate formation). Taylor et al. (1979) illustrated variations in the oxygen isotope composition of crystallizing magma by calculating an approximate mass of wallrock melted per unit mass of crystallized cumulate, in the absence of recharge. His calculation emphasizes recognition of the energy balance inherent in the process of assimilation-fractional crystallization by identifying the ratio of mass of assimilated anatectic melt to the mass of cumulates formed during an AFC 'event'. Heat associated with magma cooling as well as heat advected to the magma body by influx of recharge magma can be added to the latent heat generated by magma crystallization.

DePaolo (1981) described a quantitative approach to modeling trace elements and isotope ratios in AFC by solving differential equations expressing conservation of mass and species with fraction of melt ( $F$ ) as the independent variable. Energy balance was not explicitly considered in this early form of AFC. In order to obtain closed-form analytical solutions to the classical AFC expressions, the ratio of the mass assimilated to the mass crystallized (defined by the symbol  $r$ ) was set equal to a constant. The tractable nature of these solutions was a critical factor in the emergence of numerous, quantitative treatments of AFC by many petrologists.

In recognition of the complex behavior that characterizes magma chambers, the effects of recharge were added to the total mass and species conservation expressions describing AFC, thereby generating total mass and species conservation expressions for AFC augmented by recharge (RAFC; DePaolo, 1985). Other variations of ‘classical’ AFC models have been proposed; among the most useful of these is the “multiple element” approach developed by Aitchison and Forrest (1994). Noting the weakness of somewhat arbitrarily setting the value of  $r$ , these authors solve mass and species conservation equations (including recharge) so that  $r$  and  $f$  (defined as the mass of material assimilated / original mass of magma) may be determined. Solutions using a variety of trace element concentrations (or isotope ratios) are then plotted, with the intersection of the  $r$ -  $f$  curves apparently representing the “true values” of these variables. The advantage of this approach is that  $r$  is not arbitrarily defined but instead independently inferred from an over-determined system of mass balance equations. The disadvantages are that the value of  $r$  determined by this procedure depends on the particular trace elements used to constrain its value, and no energy conservation constraint is imposed.

Although effort has mostly been directed at investigating solutions to mass and species conservation equations, some attention has been paid to energy balance. For example, Grove and Kinzler (1986) recognized that the amount of assimilant required to explain the composition of Medicine Lake lava flows exceeded the amount theoretically available, based simply on heat available from latent effects. The discrepancy was reconciled in the context of geologic evidence that suggested the proportion of contaminated material is small relative to the total volume of erupted lava. Thus, a large volume of basalt was available as a source of heat to melt wallrock but

only a small volume of basalt was chemically contaminated. DePaolo (1985), DePaolo et al. (1992) and Perry et al. (1993) derive equations that consider the importance of recharge, assimilation, fractional crystallization and loss of heat from the magma body by a rough accounting of conductive heat transfer. This was accomplished by defining an effective ambient crustal temperature and assuming the ratio of the rate of heat loss to the rate of cumulate formation was a constant in the range 0.5 to 1. More recently, Reiners et al. (1995), building on the earlier work of Ghiorso and Kelemen (1987) and Kelemen (1986, 1990) examined the consequences of isenthalpic assimilation-fractional crystallization using the MELTS algorithm. Their model balances the enthalpy released by cooling and solidification against that required for digestion of assimilate. They found that for basaltic magma invading and assimilating felsic crust, assimilation can lead to suppression of crystallization of plagioclase and clinopyroxene, which in turn can potentially lead to large values of  $r$ , in some cases  $>1$ . After crystallization of plagioclase and clinopyroxene commences,  $r$ -values can drop significantly, commonly to  $<1$ . Their calculation clearly demonstrates that  $r$  is not, in general, constant during an AFC 'event'. By utilizing the DePaolo equations in an iterative way, they further concluded that relatively mafic magmas that do not appear contaminated on the basis of major elements (e.g.,  $<51$  wt. %  $\text{SiO}_2$ ,  $>6$  wt. %  $\text{MgO}$ ) can, in fact, be contaminated by continental crust. The trace element and isotopic ratios of such a mafic melt therefore may not be representative of the mantle source from which they were derived. This possibility has important implications for characterizing chemical heterogeneity of mantle source regions based on the composition of basaltic lava since the usual assumption is that primitive MgO-rich, low crystallinity melts are not substantially contaminated. One concludes from these considerations that application of an energy

conservation principle can have a direct and major effect on the inferences drawn regarding petrologic processes based on geochemical data, which, in retrospect, is not surprising.

Edwards and Russell (1998) trace thermal and chemical changes in a magma body undergoing AFC by determining dissolution rates of wallrock phases and balancing enthalpy. By experimentally determining mineral dissolution rates, these authors determine the rate at which assimilant is added to a magma chamber. As a function of time, they track the amount of crystallization, the amount of assimilant incorporated (and therefore  $r$ ), the temperature change, and the major element variations (liquid lines of descent) in the magma body. They found that, depending on the mineral dissolution rates, high values of  $r$  could be achieved, particularly early in the crystallization history of the body. In addition, their analysis predicts the timescale of AFC to be weeks to years.

### **Magma Chamber-Country Rock: A Composite Thermodynamic System**

A simplified thermodynamic description of a magmatic system and its surroundings serves to outline the conceptual framework of the energy-constrained approach (Fig. 1). A system undergoing EC-RAFC is taken as a composite of three sub-systems: (1) a magma body of initial mass  $M_o$ , (2) a *finite* mass (defined self-consistently based on energy conservation) of surrounding country rock ( $M_a^o$ ), and (3) a reservoir of recharge magma that is added to the magma body sub-system during the course of an RAFC ‘event’. The cumulative amount of magma injected during the RAFC ‘event’ is  $M_r^o$ . The three part composite system is separated from its surroundings (i.e., the rest of the lithosphere) by a boundary that is closed and adiabatic. The

country rock–magma body boundary is diathermal and open, allowing exchange of enthalpy and anatectic melt. The replenishment sub-system reservoir allows recharge magma, of specific composition and enthalpy, to flow into the magma body. The chamber is filled with standing magma (a mixture of cumulates and melt in thermal and chemical equilibrium) that is stirred by the release of chemical and thermal buoyancy, by the settling of dislodged pieces of country rock, and by momentum transfer between recharge and standing magma. The magma body may have a complex compositional structure: regions may be homogeneous, exhibit continuous gradients (e.g., a compositionally stratified magma cupola), preserve compositional discontinuities or horizons, or be mixed at any of a variety of spatial scales (see for example, Oldenburg et al., 1989 for quantification of mixing). Mixing of magmas is favored in cases where steep gradients in temperature, composition and velocity are established. In systems with relatively high recharge rates, magma may become well-mixed except within relatively thin marginal chemical and rheological mixed-phase boundary layers, typically several meters to tens of meters thick (Trial and Spera, 1990). The momentum transfer induced by possible magma fountaining during recharge will also aid in mixing. When the mean recharge rate is small, the tendency for mixing is lower, and stratified (thermally and compositionally) magma horizons may develop and persist.

Enthalpy transport from magma to country rock leads to compositional modification of resident melt by fractional crystallization. Enthalpy loss due to magma cooling and crystallization will heat country rock and induce anatexis when country rock temperatures exceed the local solidus, which is a function of composition and pressure. The extent of anatectic melt formation depends on the country rock solidus, the amount of heat provided by magma cooling and crystallization, and the amount of heat available from recharge magma. Assimilation of

anatectic melt will alter the elemental and isotopic composition of melt within the magma body. By writing statements for conservation of enthalpy, mass, trace species and isotopic ratios, one can compute changes in the composition of melt as each sub-system approaches thermal and chemical equilibrium. Although in nature reaction may proceed between country rock and magma without melting, as illustrated in the work of Kelemen and co-workers (Ghiorso and Kelemen, 1987; Kelemen, 1990; Kelemen et al., 1990), it is assumed in the EC-RAFC model that *melting* of country rock and the mixing of anatectic liquids with ‘pristine’ magma is a necessary prelude to magma contamination.

### **Thermal Interaction Between Magma and Country Rock: Thermal Heuristics**

Perhaps the most fundamental interaction between magma and its surroundings is a thermal one. The main irreversibility involves the production of entropy during heat exchange between all sub-systems as thermal equilibrium is approached. Developing a general set of rules for predicting quantitative aspects of magma body thermal evolution is complicated by many factors. In this section, we discuss some of the more problematic issues as a backdrop for how these matters are dealt with in the energy-constrained models.

As a point of departure, we consider a model detailed by Bejan and Anderson (1983) that serves as an *illustration* of a coupled country rock-magma body heat transfer system. Similar models are described elsewhere (Spera, 1979; Carrigan, 1988; Bergantz, 1989, 1992; Bowers et al., 1990). In this conjugate heat transfer problem, the ambient temperature of the country rock ‘far away’ from the contact ( $T_a^\circ$ ) and the magma temperature in the interior of the magma body ( $T_m^\circ$ ) are the characteristic temperatures of the problem. The average country rock-magma

*boundary* temperature ( $T_b$ ) is determined by the relative vigor of hydrothermal convection in the country rock (which transports heat away from the contact) compared to magma convection within the magma body itself (which transports heat to the contact). The ratio  $B = k_a R d^{1/2} / k_m Ra^{1/4}$  (all parameters defined in Table 1) is the dimensionless parameter that governs the boundary temperature,  $T_b$ . When  $B$  is large, hydrothermal convection efficiently carries away heat brought to the boundary and, as a consequence, the boundary temperature remains relatively low. That is, in the limit of large  $B$ , the country rock-magma body boundary acts as a good thermal conductor and  $T_b \rightarrow T_a^o$ . An environment where this condition might prevail is in the upper crust in a region undergoing extensional shear failure as a result of tectonic forces where a vigorous hydrothermal system is established. In contrast, for small  $B$ , magmatic heat cannot be transported rapidly away from the country rock-magma contact and hence  $T_b \rightarrow T_m^o$ . In this case, the boundary is more like an adiabatic one than a diathermal one. In low permeability catazonal rocks (20-40 km depth), hydrothermal flow may be less vigorous ( e.g., Schoofs et al., 2000). In this case, the boundary margin temperature is controlled by the balance between heat convected to the magma chamber and heat conduction into country rock. In the general case, the boundary temperature  $T_b$  is given by:

$$T_b = (T_m^o - T_a^o) f(B) + 1/2 (T_m^o + T_a^o) \quad (1)$$

where the function  $f(B)$  approaches  $1/2$  as  $B \rightarrow 0$  and  $-1/2$  as  $B \rightarrow 50$ . Values of  $f(B)$  at intermediate values of  $B$  may be found in Table 1 of Bejan and Anderson (1983).



It is important to note that the extent of magmatic contamination by country rock is not a simple function of the boundary temperature but depends also on the initial country rock temperature ( $T_a^0$ ), melt productivity functions  $f_a(T)$  and  $f_m(T)$  and thermodynamic parameters such as the heat capacity and phase change enthalpies of relevant materials.

### **Magmatic-Hydrothermal Systems: Transport Modeling**

Knowledge of the dynamics of magmatic-hydrothermal systems has expanded enormously in the past quarter century. The role of chemical as well as thermal convection on magma dynamics has been explored by a variety of analytical, laboratory and numerical studies. The effects of crystals and bubbles on magma rheology and convection, as well as inferences of magma residence time based on particle (crystal and bubble) size distributions and radiogenic isotope systematics have also been addressed. Multiphase effects have been considered by incorporation of phase relations in model two or three component systems with the equations of motion, energy and material balances to account for marginal mush layers along magma body-country rock contacts, the generation of chemically induced buoyancy within such layers, and the growth of porous cumulates (Campbell and Turner, 1987; Huppert and Sparks, 1988; Oldenburg and Spera, 1991, 1992; Bergantz and Dawes, 1994; Brown et. al., 1995; Spera et. al., 1995; Raia and Spera, 1997; Barboza and Bergantz, 1997, 1998). Similarly, models of hydrothermal convection have also progressed in the last quarter-century. Complexities associated with medium anisotropy, heterogeneous permeability fields, salinity and thermally-driven buoyancy, the effects of topography, variations in the thermodynamic and transport properties of  $H_2O-CO_2-NaCl$  fluids,

and the role played by metamorphic fluids from prograde reactions have been addressed. Based on extensive geochemical investigations, H.P. Taylor and colleagues (e.g., Criss and Taylor, 1986 and references cited within) have pointed out important differences in the behavior of meteoric-hydrothermal systems depending upon magma composition and temperature.

It is clear from collective study of these works that any attempt to track the chemical evolution of magma bodies which neglects thermal budgets and the energetics of partial melting is inchoate. The extent of chemical interaction and chemical evolution of magma is inextricably bound to the thermal interaction amongst the composite sub-systems. The irreversible production of entropy implied by heat exchange between sub-systems in RAFC interactions allows one to define a temperature, the equilibration temperature ( $T_{eq}$ ), as a natural ‘progress’ variable to describe the approach to equilibrium during the irreversible process of heat exchange (Prigogine, 1962). Because the eruptive temperature of magma can be directly measured or estimated from geothermometry, it is sensible to utilize magma temperature as the independent variable in EC-RAFC modeling.

### **Extraction of Anatectic Melt**

How efficiently is anatectic melt extracted from its source host and added to the standing magma body? This question is central to petrogenetic models that attempt to predict the geochemical fingerprint of anatexis. Heat and material exchange can be de-coupled if anatectic melts are generated but not mixed into the magma body sub-system. Hence it is essential to discuss the efficacy of melt extraction before detailing EC-RAFC and EC-AFC models.

The processes whereby melt is extracted from partially molten host rock are complex and remain imperfectly known despite considerable research in the past quarter century (Arzi, 1978; van der Molen and Paterson, 1979; Shaw, 1980; Richter and McKenzie, 1984; McKenzie, 1984, 1985; Fowler, 1985; Richter, 1986; Ribe, 1985, 1987; Sleep, 1987; Scott, 1988; Scott and Stevenson, 1989; Stevenson, 1989; Bergantz, 1989; Riley et al., 1990; Riley and Kohlstedt, 1991; Takahashi, 1992; Hart, 1993; Bergantz and Dawes, 1994; Daines and Kohlstedt, 1994, 1997; Sawyer, 1994; Brown et al., 1995; Petford, 1995; Rushmer, 1995; Rutter and Neumann, 1995; Kohlstedt and Zimmerman, 1996; Connolly et al., 1997; Barboza and Bergantz, 1998; Petford and Koenders, 1998; Zimmerman et al., 1999). There are two general models for the description of melt segregation: percolative and melt-vein. These are 'end-member' models and reality is likely to incorporate elements of both. In percolation models, the matrix or residual solid is considered a granular, deformable material of isotropic and uniform permeability. Melt is segregated from the deformable matrix at rates that depend on the balance amongst capillary, gravity and viscous forces. The compaction length  $\lambda_c$  (McKenzie, 1984) gives the length scale over which the deformation must occur in order that Darcy pressure balances compaction forces:

$$\lambda_c = \left( \frac{K}{\eta_a} \right)^{1/2} \quad (2)$$

where  $\eta_a$ ,  $K$  and  $\lambda_c$ , represent the effective viscosity of the matrix, the permeability (a function of grain size and porosity) and the viscosity of anatectic melt. If the region of partial fusion is significantly larger than  $\lambda_c$ , melt segregation is governed by the balance between buoyancy and

Darcy friction. The permeability is notoriously difficult to estimate. Experiments by Riley et al. (1990) suggest an expression of the form  $K = d_o^2 f_a^n / b$  where  $d_o$  is a typical grain size,  $f_a$  the melt fraction,  $n \sim 1$  and  $b \sim 5 \times 10^3$ . For values appropriate to crustal anatexis ( $f_a = 0.2$ ,  $d_o = 3\text{mm}$ ,  $g = 9.8 \text{ ms}^{-2}$ ,  $\rho = 300 \text{ kg/m}^3$ ,  $\eta = 10^{18} \text{ Pa s}$  and  $\eta_a \sim 10^5 \text{ Pa s}$ ),  $K = 4 \times 10^{-11} \text{ m}^2$  and  $u_c = 20\text{m}$ . The relative vertical velocity between melt and matrix ( $u$ ) is then given by:

$$u = K(1 - f_a)g / \eta_a f_a \quad (3)$$

where  $\rho$  represents the density difference between solid and melt. The velocity of melt relative to restite is of order 150 m/Ma. According to the percolative model, a thin (tens of meters on average) selvage of country rock could be drained on a  $10^5$  yr timescale. In the mantle where the melt viscosity is quite low ( $\eta_a = 1 \text{ Pa s}$ ), the percolative model gives extraction rates  $10^5$  times higher, essentially geologically instantaneous. Short-lived radioisotope studies are consistent with such high melt extraction efficiencies for partial melting of peridotitic sources to generate basaltic magma.

The melt-vein model for melt segregation, perhaps more applicable to melting of non-peridotitic sources, gains support from field, laboratory and fluid dynamical studies. This scenario may be more geologically realistic in light of the heterogeneous and anisotropic nature of most source regions. The essential insight is that melt accumulates in discrete veins or pods, of the order cm in length, oriented parallel to the axis of minimum effective stress during shear deformation associated with intrusion of partially-molten material. There is clear field and

laboratory evidence that extensional shear failure is associated with melt mobilization (e.g., Shaw, 1980; Spera, 1980). Once veins grow large enough, an interconnected critical drainage network may develop so that melt can be transported at rates  $\sim 1$  mm/s (30 km/yr) or greater in response to small differential stresses. These rates are much greater than those characterizing Darcy percolative flow. Laboratory experiments on crystal-melt suspensions often exhibit small-scale melt redistribution in response to surface forces and small deviatoric stresses (van der Molen and Patterson, 1979; Cooper and Kohlstedt, 1986). The total volume of melt that can exist in a drainage network depends upon the volume of the partially molten region and the details of the distribution of crack apertures, lengths and widths as well as the orientation of the local stress field including but not restricted to thermal stresses. Presumably each magma-country rock interaction is unique. Once a critical level of connectivity exists amongst melt-filled fractures, relatively rapid drainage of the fracture plexus can occur as the effective (equivalent) permeability dramatically increases. Petford and Koenders (1998) proposed a phenomenological model for self-organization and fracture connectivity created by thermal stresses generated by intrusion of hot magma into cooler ambient country rock. They estimate transient permeability in the range  $10^{-10}$  to  $10^{-5}$  m<sup>2</sup>, many orders of magnitude greater than in the percolative model. The permeability (K) is related to the fracture connectivity ( ) by Gueguen and Dienes (1989) in a fracture model according to:

$$K=4 A^3 n_0c^5 \quad (4)$$

where  $A$  is the fracture aspect ratio,  $n_o$  ( $1/l^3$ ) is the fracture number density (where  $l$  is the fracture spacing), and  $c$  is the fracture length. Theory enables estimation of  $K$  which changes dramatically as the ratio of connected to unconnected nodes in the percolation network varies from zero to unity. As a scale permeability, consider  $A = 0.1$ ,  $l = 0.5\text{m}$ ,  $c = 0.1\text{m}$  and  $\phi = 0.2$ . This gives  $K \sim 10^{-8} \text{ m}^2$ , considerably larger than the classical Darcy estimate ( $K = d_o^2 f_a^n / b$ ) of  $10^{-11} \text{ m}^2$ .

For the purposes of this study, we parameterize the extraction of anatectic melt from its source (country rock) by defining a melt extraction efficiency ( $\eta$ ) defined as the fraction of melt *delivered* to the magma body relative to mass generated in the country rock ( $M_a^*$ ). Dimensional analysis shows that  $\eta$  depends on the melt viscosity, magnitude and orientation of deviatoric stresses, dimensions of typical cracks (apertures, crack lengths and widths) and the crack number density. Wholesale digestion of stoped country rock (Walker and Kiefer, 1985) is another way anatectic melt and hydrothermal fluids can enter a magma body. Further discussion of the efficiency of anatectic melt extraction may be found in Ashworth and Brown, (1990) and Rubie and Brearley, (1990). Wickham (1990) has made some important arguments regarding evidence from Sr and O isotopes and their redistribution during anatexis. Vielzeuf and Holloway (1988) discuss melt production in pelitic sources. Hart (1993) concludes that melt generated by anatexis of upwelling peridotitic mantle experiences only limited diffusive reequilibration based on a fractal network-melt channel model similar to the one discussed here.

Because of the difficulty in assessing the extent of melt extraction in a general way,  $\eta$  is set equal to unity in the EC-AFC expressions below and in the examples presented in Bohrsen and Spera (2000, this volume). By setting  $\eta = 1$ , the geochemical effects of contamination are

*maximized* since all melt produced during anatexis acts as a chemical contaminant and not just energy sink.

## **EC-RAFC AND EC-AFC MODEL FORMULATIONS**

### **EC-RAFC Model Formulation**

In the EC-RAFC model, a mass of magma  $M_o$  at initial temperature  $T_m^o$  is injected into crust at temperature  $T_a^o$  (Fig. 1). Both magma and crust have unique initial trace element ( $C_m^o, C_a^o$ ) and isotopic ( $\delta_m^o, \delta_a^o$ ) compositions. Recharge magma of mass  $M_r$  with distinct initial trace element ( $C_r^o$ ) and isotopic ( $\delta_r^o$ ) composition and initial temperature ( $T_r^o$ ) is added to original magma according to some *a priori* defined relation  $M_r = f(T_m)$  such that total mass injected during the RAFC ‘event’ equals  $M_r^o$ . The constraint imposed by enthalpy balance is that heat associated with cooling and crystallization of original magma and recharge magma is matched with the enthalpy requirements for heating and partial melting of country rock. The amount of country rock involved in the interaction ( $M_a^o$ ) uniquely follows upon specification of the equilibration temperature,  $T_{eq}$ , which is set *a priori*. Country rock partial melts are partially or completely extracted, added to and thermally homogenized with the molten portion of the standing magma body. Conservation of enthalpy enables one to track the mean temperature of country rock restite ( $T_a$ ) as a function of the melt temperature ( $T_m$ ) during the approach to the common equilibrium temperature ( $T_{eq}$ ). At each step in the approach to  $T_{eq}$ , local thermal equilibrium is maintained among cumulates, magma in the chamber, recharge magma, and the newly added mass

of assimilant. This means that assimilated country rock melt and recharge magma are brought to the local and common temperature  $T_m$ . The calculation is continued until  $T_m$  and  $T_a$  equal  $T_{eq}$ .

Latent heat effects are treated by adopting a single effective fusion ( $h_{fus}$ ) or crystallization ( $h_{cry}$ ) enthalpy computed as a weighted average for the mixture of phases involved in the phase transition. Values of fusion enthalpies for a number of phases are given in Table 2. It is assumed that enthalpy is released uniformly throughout the melting or crystallization interval, which is defined by the temperature difference between the liquidus ( $T_{l,m}$  or  $T_{l,a}$ ) and solidus temperature ( $T_s$ ). This is an approximation; representative calculations accomplished using the MELTS algorithm (Ghiorso and Sack, 1995; Ghiorso, 1997) indicate that crystallization intervals do not vary widely during AFC. Sensible contributions to the enthalpy balance are computed using average specific isobaric heat capacities calculated from available thermodynamic data (Table 3). Although the temperature dependence of the isobaric heat capacity of silicate materials is well known, this level of detail is likely to be of second-order importance.

The solution of the balance equations representing conservation of energy, mass and species provides self-consistent values for the mass of heated country rock (restite) plus partially molten country rock involved in the RAFC process ( $M_a^o$ ), the amount of assimilant partial melt ( $M_a^*$ ) (some portion of  $M_a^o$ ), the mass of melt in the chamber ( $M_m$ ), the total amount of recharge magma ( $M_r$ ) and the mass of cumulates ( $M_c$ ) as a function of the magma temperature  $T_m$  along the path  $T_m^o \rightarrow T_{eq}$ . Simulation results also include the trace element ( $C_m$ ) and isotopic ( $\delta_m$ ) composition of contaminated magma as well as the trace element composition ( $C_c$ ) of cumulates. Because of the hierarchical nature of the EC-RAFC formulation, compositionally distinct melt



reservoirs *within* the melt portion of the magma body can be accounted for. However, in most cases so little is known regarding the structure of melt compositional heterogeneity, this level of detail seems unwarranted.

The equilibration temperature,  $T_{eq}$ , is used to parameterize a particular RAFC evolution in geochemical space.  $T_{eq}$  characterizes the overall extent of interaction between magma and country rock and is related to  $T_b$  discussed earlier. For  $T_b$  approaching  $T_m^o$ , the  $T_{eq}$  of the RAFC ‘event’ is relatively high, and the mass of country rock ( $M_a^o$ ) involved in the RAFC process is relatively small (although the fraction  $M_a^*/M_a^o$  may be large). In this case, the thermal effects of injected magma do not extend great distances from the contact into country rock because of poor effective heat conductivity. In contrast, if  $T_b$  is low (e.g., rapid hydrothermal heat advection in an epizonal environment),  $M_a^o$  is larger but a smaller fraction  $M_a^*/M_a^o$  is formed. In the case  $T_{eq} = T_s$ , the country rock temperature ( $T_a$ ) does not exceed the solidus (on average), and assimilation of anatectic melts is not important. An appropriate  $T_{eq}$  can often be estimated by geological considerations, thus linking the model with geologically relevant data. For example, in reconstruction of petrogenetic processes in a volcanic system characterized by a spectrum of compositions, one would naturally choose  $T_{eq}$  less than or equal to the eruptive temperature of the most evolved composition. In contrast, if the magmatic system under study is characterized by limited compositional variation,  $T_{eq}$  may be close to but somewhat less than  $T_m^o$ .  $T_{eq}$  is used as the independent parameter in the EC-RAFC model because it provides an intuitive measure of the extent of thermal interaction of country rock and magma. Additionally, the irreversible

production of entropy, generated mainly by dissipation of magmatic heat, is directly related to  $T_{\text{eq}}$ .

### **EC-AFC Model Formulation**

In the remainder of this paper, we consider only the process of assimilation-fractional crystallization; recharge has been set identically to zero to highlight the constraints imposed purely by energy conservation and partial melting on assimilation of anatectic melts. Future work will delineate the mathematics and applications of EC-RAFC. In the following sections, the differential equations expressing conservation of energy, mass and species as well as initial conditions and parameters of the model are presented. A derivation of these equations along with a description of the algorithm used to model an EC-AFC ‘event’ is presented in Appendix I. All symbols are defined in Table 1.

#### *EC-AFC Mathematical Model*

The description of the EC-AFC model comprises two parts. The first is an integral calculation defining a relationship between  $T_{\text{eq}}$  and  $M_a^0$  for a particular set of thermal parameters (heat capacity, latent heats, liquidii of magma and country rock, melting functions) and initial conditions ( $T_a^0$ ,  $T_m^0$ ). The second describes the energy-constrained thermal and geochemical path followed by a batch of magma during approach to  $T_{\text{eq}}$ . For a particular set of thermal parameters and initial conditions, each  $T_{\text{eq}}$  is associated with a unique  $M_a^0$  which is required to solve the path-dependent differential equations describing the chemical and thermal evolution of the magma body.

*Integral Balance* The integral enthalpy balance provides an essential constraint on the geochemical path followed as initially pristine melt cools, crystallizes and assimilates anatectic liquid. The balance can be represented as an algebraic relationship between the mass of country rock involved in the thermal interaction ( $M_a^o$ ) and the equilibration temperature ( $T_{eq}$ ), the independent variable in the EC-AFC formulation. Note that not all of  $M_a^o$  may actually melt, although all of it does eventually come to thermal equilibrium ( $T_{eq}$ ) with magma. The extent of country rock melting depends on the temperature-melt productivity relation,  $f_a(T_a) = M_a^*/M_a^o$  where  $M_a^*$  is the mass of country rock that partially melts and is incrementally added to the batch of pristine magma, of initial mass  $M_o$ , undergoing simultaneous fractional crystallization. Energy conservation incorporates heating and partial melting of country rock, magma cooling and formation of cumulates self-consistently. The parameters include the melt production functions for country rock and magma ( $f_a$  and  $f_m$ , respectively), enthalpy of crystallization for magma ( $h_{cry}$ ), the fusion enthalpy for country rock ( $h_{fus}$ ) and the average isobaric specific heat capacity of magma ( $C_{p,m}$ ) and assimilate ( $C_{p,a}$ ). The relationship may be expressed in terms of  $M_a^o$  as a function of  $T_{eq}$ :

$$\bar{M}_a^o = \frac{C_{p,m}(T_m^o - T_{l,m}\bar{T}_{eq}) + h_{cry}(1 - f_m(\bar{T}_{eq}))}{C_{p,a}(T_{l,m}\bar{T}_{eq} - T_a^o) + h_{fus}f_a(\bar{T}_{eq})} \quad (5)$$

Overbars represent dimensionless variables. Note that  $f_a(T)$  is the mass fraction of anatectic melt as a function of temperature *for the bulk composition of the country rock*;  $f_m(T)$  is the analogous

temperature-dependent production function for original (pre-contaminated) magma. These are *a priori* estimates of the fraction of melt as a function of temperature for pristine magma and wall rock. A common solidus temperature ( $T_s$ ) is identified. Because independent nonlinear melt-production functions are defined for magma and country rock, identification of a common solidus temperature is not a limitation of the model. The liquidus of country rock and unmodified magma are equal to  $T_{l,a}$  and  $T_{l,m}$ , respectively. Liquidus temperatures are based on laboratory experiments or from MELTS (Ghiorso, 1997) simulations and are chosen to account for differences in bulk composition independent of the EC-AFC model *per se*.

*Geochemical and Thermal Path* To compute the thermal, trace element and isotopic path of melt within the magma (melt plus cumulate) sub-system, a system of coupled ordinary differential equations expressing conservation of enthalpy, mass, species and isotopic composition is solved. The temperature of the country rock restite ( $T_a$ ), the mass of assimilant that partially melts ( $M_a^*$ ), the fraction of melt ( $M_m$ ) within the magma body, the mass of cumulates ( $M_c$ ) crystallized and the concentration of trace elements in melt ( $C_m$ ) and crystalline cumulates ( $C_c$ ) are computed self-consistently. The isotopic compositions of radiogenic elements ( $\delta_m$ ) and of oxygen ( $\delta_m$ ) in the melt are determined as well. The independent variable is the melt temperature ( $T_m$ ), and the calculation ends when the equilibration temperature ( $T_{eq}$ ), set *a priori* by the investigator, is attained. We emphasize that  $T_{eq}$  must be specified in order to compute the path in temperature-composition space because  $M_a^0$ , the mass of country rock involved in the EC-RAFC 'event', is a function of  $T_{eq}$ . Although the reason for setting the calculation this way may

appear arcane, a windfall arises from the flexibility of the scheme when applied to real systems, which, after all, are highly variable in conformation.

The model consists of  $2+t+i+s$  differential equations where  $t$  is the number of trace elements,  $i$  the number of radiogenic isotopic ratios and  $s$  the number of stable isotopes considered in the calculation. There are no limitations on  $t$ ,  $s$  or  $i$ . Pressure is not accommodated explicitly in the current generation of EC-AFC models although adjustment of liquid and the solidus temperatures can be made to simulate variations in pressure. A full treatment of major phase relations assuming local thermodynamic equilibrium would improve the predictive capabilities of the model.

The first differential equation expresses conservation of energy along the path as country rock heats up, partially melts and thermally equilibrates with melt from the magma body. Energy conservation leads to a differential expression for the country rock restite temperature ( $T_a$ ) as a function of the magma temperature  $T_m$ . Anatectic melt, generated as country rock temperature ( $T_a$ ) exceeds the solidus ( $T_s$ ), is assumed to rapidly mix both compositionally and thermally with standing magma. Note that along the equilibration path, restite (i.e., the crystalline part of the country rock) is not immediately brought into thermal equilibrium with magma whereas anatectic melt is brought to local thermal equilibrium with standing magma. It is possible to allow for incomplete extraction of anatectic melt by introduction of an extraction efficiency factor ( $\epsilon$ ). In this study, we adopt the approach that all anatectic melt finds its way into the magma body (i.e.,  $\epsilon=1$ ). For cases where  $T_{eq}$  is less than  $T_{l,a}$ , the thermal equilibrium condition is  $T_a=T_m=T_{eq}$ .

When  $T_{eq}>T_{l,a}$ , the equilibrium condition is that  $T_m=T_{eq}$  since no restite remains (i.e., all

wallrock has been melted). The differential equation gives the derivative of the restite temperature  $T_a$  with respect to the magma temperature  $T_m$  along the path towards thermal equilibrium at  $T_{eq}$ :

$$\frac{d\bar{T}_a}{d\bar{T}_m} = \frac{-1}{\bar{M}_a^o} \frac{T_{l,m} C_{p,m} + h_{cry} f'_m(\bar{T}_m) + C_{p,a} T_{l,m} \bar{M}_a^o f'_a(\bar{T}_a)}{T_{l,m} C_{p,a} (1 - f_a(\bar{T}_a)) + h_{fus} f'_a(\bar{T}_a) + C_{p,a} (\bar{T}_m - \bar{T}_a) T_{l,m} f'_a(\bar{T}_a)} \quad (6)$$

where  $f'_a$  and  $f'_m$  represent derivatives of the melt production functions with respect to  $T_a$  and  $T_m$ , respectively.

The second constraint is a statement of conservation of total mass. The derivative of the mass of *melt* in the magma body ( $M_m$ ) with respect to the magma temperature is expressed in terms of melt production functions and their derivatives and uses the constraint imposed by energy conservation. The mass of melt in the magma body along the path is related to the amount of melt initially present before the AFC ‘event’ ( $M_o$ ), the amount added by assimilation of anatectic melt ( $M_a^*$ ) and the amount removed by cumulate formation ( $M_c$ ). The expression has the differential form:

$$\frac{d\bar{M}_m}{d\bar{T}_m} = \bar{M}_a^o f'_a(\bar{T}_a) \frac{d\bar{T}_a}{d\bar{T}_m} + f'_m(\bar{T}_m) \quad (7)$$

where the prime on  $f_a$  and  $f_m$  denotes a temperature derivative.

Conservation of species provides the basis for defining the mass concentration of a trace element in the melt as a function of the melt temperature,  $T_m$ . Concentration of the trace element

in the country rock is denoted by  $C_a$ . We assume that partial melting of country rock is described by fractional melting so that the concentration of trace element in anatectic melt is given by:

$$\bar{C}_a = \frac{1}{D_a} \left(1 - f_a(\bar{T}_a)\right)^{\frac{D_a-1}{D_a}} \quad (8)$$

where  $D_a$  is a function of composition and temperature (see Appendix I). Additionally, a distinct melt-solid partition coefficient  $D_m$ , possibly dependent upon composition and temperature, is defined so that the fractionation of trace elements between cumulates and melt can be accounted for according to fractional crystallization. With these auxiliary expressions, the species balance expression takes the form:

$$\frac{d\bar{C}_m}{d\bar{T}_m} = \frac{1}{\bar{M}_m} \bar{M}_a^o (s\bar{C}_a - \bar{C}_m) f'_a(\bar{T}_a) \frac{d\bar{T}_a}{d\bar{T}_m} + \bar{C}_m (D_m - 1) f'_m(\bar{T}_m) \quad (9)$$

For an isotopic ratio  $r_m$ , the differential equation becomes:

$$\frac{d r_m}{d\bar{T}_m} = \frac{1}{\bar{M}_m} s \frac{\bar{C}_a}{\bar{C}_m} \left( r_a^o - r_m \right) \bar{M}_a^o f'_a(\bar{T}_a) \frac{d\bar{T}_a}{d\bar{T}_m} \quad (10)$$

where  $\bar{a}^o$  and  $\bar{a}_m$  represent the isotopic ratio in anatectic melt (identical to country rock) and in the melt (at temperature  $T_m$ ), respectively. Radiogenic in-growth has been neglected and no isotopic fractionation upon melting or crystallization is allowed.

Finally, the differential equation expressing oxygen isotope balance may be written:

$$\frac{d\bar{a}_m}{dT_m} = \frac{1}{M_m} \left( \bar{a}^o - \bar{a}_m \right) k_{oxy} \bar{M}_a^o f_a \left( \bar{T}_a \right) \frac{d\bar{T}_a}{dT_m} \quad (11)$$

Temperature-dependent oxygen fractionation is neglected in (11); this effect is generally small in magmatic systems and is of order one or two per mil. In cases where magma and country rock have nearly the same oxygen isotopic ratio, temperature effects may be important to consider and (11) should be modified.

*Initial conditions* Equations (6), (7), (9), (10) and (11) constitute an initial value problem with  $T_m$  as the independent variable. This set of  $2+t+i+s$  coupled ordinary differential equations is subject to the following initial conditions: at  $T=T_m^o$ ,  $T_a=T_a^o$ ,  $M_m=M_o$ ,  $C_m=C_m^o$  for  $t$  trace element species,  $\bar{a}_m = \bar{a}_m^o$  for  $i$  isotope species including  $\bar{a}_m = \bar{a}_m^o$  for oxygen. The system of differential equations is numerically solved by a fourth-order Runge-Kutta method once cast into dimensionless form (see Appendix I).

## CONCLUSIONS



The geochemical evolution of a batch of magma is intimately tied to interactions with its environment. Open system behavior (e.g., assimilation and magma replenishment) is more the rule than the exception as magma moves between source and surface. The open system processes of magma replenishment, assimilation and fractional crystallization can be formulated as a coupled set of  $3+t+i+s$  non-linear ordinary differential equations with magma temperature as the independent variable where  $t$  is the number of trace elements,  $i$  is the number of isotopic ratios and  $s$  is the number of stable isotope ratios treated in the simulation of the geochemical path. In this paper, explicit formulation of EC-AFC has been derived. Inclusion of an energy conservation principle constrains the trace and isotopic evolution of magma system more tightly than ‘classical’ AFC models because the initial thermal state of the surroundings and the thermodynamic properties of silicates are self-consistently accommodated. In the accompanying paper (Bohrson and Spera, 2000, this volume) the EC-AFC formulation is applied to a number of natural systems. Detailed quantitative comparison between ‘classical’ AFC and EC-AFC geochemical paths highlights some remarkable and significant differences in trace element-isotope ratio coordinates for many instances. The single most important and in some sense obvious conclusion of this work is that the energetics of petrologic processes must be explicitly accounted for in study of complex RAFC phenomena. RAFC without self-consistent application of energy conservation is like an automobile without an engine. A user-friendly program that runs on a PC or a Mac and requires Excel 98 is available at <http://magma.geol.ucsb.edu/research/recharge.html>.

## APPENDIX I: DERIVATION OF EC-AFC EQUATIONS

### Integral Energy Balance

The model posits that the enthalpy required for heating and partial melting of country rock (the heat absorbed) is balanced by the heat liberated by cooling and crystallization (cumulate formation) of magma. It is necessary to select a final or equilibration temperature ( $T_{eq}$ ) in order to define an EC-AFC ‘event’. Once  $T_{eq}$  is picked, application of energy conservation provides a relationship between the total mass of country rock ( $M_a^o$ ) involved in the magma-host thermal interaction and the chosen equilibration temperature,  $T_{eq}$ . Enthalpy available for heating and partial melting comes from the sensible heat associated with cooling of magma of mass  $M_o$  from initial temperature  $T_m^o$  to  $T_{eq}$  and the latent heat ( $h_{cry}$ ) liberated by formation of cumulates of mass  $M_c = [1 - f_m(T)] M_o$ . The enthalpy of crystallization and isobaric heat capacity are taken as constants and the temperature-melt fraction relation (also known as the melt productivity),  $f_m(T)$ , is a function of temperature and is obtained by independent phase equilibria experiments or MELTS modeling. We have found the MELTS simulator to be especially handy for determining liquid and solid and bulk distribution coefficients,  $D_a$  and  $D_m$  for different starting materials. The integral expression for heat liberated is:

$$h_{lib} = M_o f_m(T_{eq}) C_{p,m}(T_m^o - T_{eq}) + M_o (1 - f_m(T_{eq})) (C_{p,m}(T_m^o - T_{eq}) + h_{cry}) \quad (A1)$$

Enthalpy is absorbed by country rock of mass  $M_a^o$  as it heats up and undergoes partial fusion, provided the local country rock temperature ( $T_a$ ) exceeds the solidus ( $T_s$ ). The initial temperature of country rock is  $T_a^o$ , and the entire mass is brought to the equilibration temperature  $T_{eq}$ . The fraction of partial melt in the country rock is defined by the melt production function  $f_a(T)$ , which is analogous to  $f_m(T)$  defined above. The mass of anatectic melt, a quantity that grows during the EC-AFC ‘event’, is defined as  $M_a^*$ . The heat of fusion ( $h_{fus}$ ) required for melting is taken as a constant. The integral expression for the heat absorbed by country rock becomes:

$$h_{abs} = M_a^o \left( 1 - f_a(T_{eq}) \right) C_{p,a} (T_{eq} - T_a^o) + f_a(T_{eq}) M_a^o \left( C_{p,a} (T_{eq} - T_a^o) + h_{fus} \right) \quad (A2)$$

By equating the total heat liberated to the heat absorbed,  $M_a^o$  the total mass of country rock that thermally equilibrates with mass  $M_o$  of magma, may be computed as a function of  $T_{eq}$  according to:

$$\bar{M}_a^o = \frac{C_{p,m} T_{l,m} (\bar{T}_m^o - \bar{T}_{eq}) + h_{cry} (1 - f_m(\bar{T}_{eq}))}{C_{p,a} T_{l,m} (\bar{T}_{eq} - \bar{T}_a^o) + f_a(\bar{T}_{eq}) h_{fus}} \quad (A3)$$

In (A3) and the expressions that follow, dimensionless quantities are denoted by an overbar.

Non-dimensional parameters are defined along with other terms in Table 1. Recall that  $M_o$  is the

original mass of magma at  $T_m^0$  at the start of the EC-AFC ‘event’. The temperature  $T_{l,m}$  is used to non-dimensionalize the country rock restite and magma chamber melt temperature ( $T_a$  and  $T_m$ , respectively). Concentrations are scaled to the initial concentrations in magma ( $C_m^0$ ) and country rock assimilate ( $C_a^0$ ), before partial melting. The fraction of the system that is melt ( $M_m$ ) at any point is scaled by  $M_0$  which also is used to scale both  $M_a^0$  and  $M_a^*$ , where  $M_a^0$  is the entire mass of country rock involved in the ‘event’ and  $M_a^*$  is the mass of the country rock that melts and is added during the AFC ‘event’. The non-dimensional mass of melt ( $\bar{M}_m$ ) is equivalent to the fraction of melt in the magma body sub-system.

### **Geochemical and Thermal Path**

Once  $M_a^*$  has been computed algebraically at the specified  $T_{eq}$ , the differential equations defining the geochemical and thermal path may be solved. Energy conservation for each incremental step along the EC-AFC path enables determination of restite temperature ( $T_a$ ) as a function of the melt temperature ( $T_m$ ). We adopt the convention that absorbed heat is positive. Energy conservation demands that  $h_{lib} + h_{abs} = 0$ ; differentiation with respect to the melt temperature  $T_m$ , application of the chain rule and rearrangement give the following form for the variation of  $T_a$  (restite temperature) with respect to  $T_m$  (melt temperature):

$$\frac{d\bar{T}_a}{d\bar{T}_m} = - \frac{dh_{lib}/d\bar{T}_m}{dh_{abs}/d\bar{T}_a} \quad (A4)$$

The differential forms for liberated and absorbed heat are:

$$\frac{dh_{lib}}{d\bar{T}_m} = -\left(T_{l,m} C_{p,m} + h_{cry} f'_m(\bar{T}_m) + \bar{M}_a^o T_{l,m} C_{p,a} f'_a(\bar{T}_a)\right) \quad (A5a)$$

$$\frac{dh_{abs}}{d\bar{T}_a} = \bar{M}_a^o \left(T_{l,m} C_{p,a} (1 - f_a(\bar{T}_a))\right) + \left(T_{l,m} C_{p,a} (\bar{T}_m - \bar{T}_a) + h_{fus}\right) f'_a(\bar{T}_a) \quad (A5b)$$

Substitution of (A5a) and (A5b) in (A4) gives the required expression written in non-dimensional form:

$$\frac{d\bar{T}_a}{d\bar{T}_m} = \frac{-1}{\bar{M}_a^o} \frac{T_{l,m} C_{p,m} + h_{cry} f'_m(\bar{T}_m) + T_{l,m} C_{p,a} \bar{M}_a^o f'_a(\bar{T}_a)}{T_{l,m} C_{p,a} (1 - f_a(\bar{T}_a)) + h_{fus} f'_a(\bar{T}_a) + T_{l,m} C_{p,a} (\bar{T}_m - \bar{T}_a) f'_a(\bar{T}_a)} \quad (A6)$$

By convention  $h_{fus}$  and  $h_{cry}$  are positive numbers and primes denote differentiation with respect to  $T_m$  or  $T_a$  as appropriate.  $T_a$  is computed so long as  $T_a < T_{l,m}$ ; for  $T_a \geq T_{l,m}$  country rock is entirely molten (no restite remains),  $M_a^* = M_a^o$  and the single relevant temperature is  $T_m$ .

Conservation of total mass gives rise to a differential form for the variation of melt mass ( $M_m$ ) with melt temperature ( $T_m$ ):

$$\frac{d\bar{M}_m}{d\bar{T}_m} = \bar{M}_a^o f'_a(\bar{T}_a) \frac{d\bar{T}_a}{d\bar{T}_m} + f'_m(\bar{T}_m) \quad (A7)$$

$M_m$  is the fraction of melt in the magma body as it evolves along the EC-AFC path towards

equilibrium. The mass fraction  $M_m$  is scaled by the original (pristine) mass of magma ( $M_o$ ), and is identical to the parameter  $F$  used in classical AFC formulations (e.g., DePaolo, 1981).  $M_m$  evolution accounts for the addition of anatectic melts as well as the removal of melt by formation of cumulates at each incremental step along the EC-AFC path.  $M_m$  also accounts self-consistently for the energetics of country rock partial melting, solidification of cumulates, and sensible heat effects in both the country rock and magma body sub-systems. Note that temperature-derivatives of the melt productivity functions  $f_a$  and  $f_m$  are evaluated at temperatures  $T_a$  and  $T_m$ , respectively in (A7) in order to correctly follow the variation of  $M_m$  as  $T_m \rightarrow T_{eq}$ .

Trace element conservation enables one to write a differential equation for the concentration of trace element in the melt as a function of  $T_m$ . This balance models addition of trace element into magma chamber melt associated with partial melting (fractional fusion in the country rock) and removal of trace element by fractional crystallization of cumulates. The fractional melting model is:

$$\bar{C}_a = \frac{C_a}{C_a^o} = \frac{1}{D_a} \left(1 - f_a(\bar{T}_a)\right)^{(1-D_a)/D_a} \quad (\text{A8})$$

where  $D_a$  is the distribution coefficient (the equilibrium constant of the trace element distribution reaction) between anatectic melt and residual restite. Trace element equilibrium constants are taken as functions of temperature:

$$D_a = D_a^o \exp \frac{-H_a}{RT_{l,m}} \frac{1}{\bar{T}_a} \quad (\text{A9a})$$

$$D_m = D_m^o \exp \frac{-H_m}{RT_{l,m}} \frac{1}{\bar{T}_m} \quad (\text{A9b})$$

In (A9),  $H_a$  and  $H_m$  represent the *effective* enthalpies of the reactions governing bulk partitioning of trace element between anatectic melt and country rock restite (A9a) and between magma chamber melt and cumulates (A9b), respectively. The  $H$  values are ‘effective’ values in the sense that the dependence of  $D_a$  and  $D_m$  on bulk composition is parameterized using the temperature dependence of  $D_a$  and  $D_m$ . The ‘effective’ values  $H_a$  and  $H_m$  are chosen independently of the EC-AFC model by consideration of phase equilibria relevant to appropriate bulk compositions and temperatures incurred during the AFC ‘event’. Constant bulk partition coefficients are modeled by setting  $H_a$  and  $H_m$  identically to zero. With these auxiliary relations, trace element conservation in the melt ( $C_m$ ) as a function of melt temperature ( $T_m$ ) is:

$$\frac{d\bar{C}_m}{d\bar{T}_m} = \frac{1}{\bar{M}_m} \bar{M}_a^o (s\bar{C}_a - \bar{C}_m) f_a'(\bar{T}_a) \frac{d\bar{T}_a}{d\bar{T}_m} + \bar{C}_m (D_m - 1) f_m'(\bar{T}_m) \quad (\text{A10})$$

where  $s = C_a^o/C_m^o$ .

The isotopic evolution of melt is calculated by neglecting radiogenic ingrowth and assumes isotopic equilibrium between magma body melt and cumulates. Similarly, anatectic melt is assumed to be in isotopic equilibrium with the country rock. Anatectic melt becomes thermally mixed and chemically homogenized with magma body melt instantaneously upon addition. One could introduce a parameter to allow for incomplete mixing and melt extraction as well as isotopic

disequilibrium between anatectic melt and its source rock. Unfortunately, there is little to constrain these possibilities in a general way. The isotope balance expression becomes:

$$\frac{d\bar{T}_m}{d\bar{T}_a} = \frac{1}{M_m} \left( \bar{C}_a - \bar{C}_m \right) \bar{M}_a f_a(\bar{T}_a) \frac{d\bar{T}_a}{d\bar{T}_m} \quad (\text{A11})$$

where  $\bar{C}_a$  and  $\bar{C}_m$  represent the isotopic ratio for anatectic and magma chamber melt, respectively.

Finally, a stable isotope balance may be written. We neglect temperature dependent isotopic effects and specifically write the balance for oxygen isotopes, which are of widespread use in geochemical investigations. For lighter isotopes, such as D/H, thermal fractionation is important and (A12) would have to be modified. Even for oxygen there is a small (circa 1 per mil) temperature fractionation effect that should be kept in mind. However, in most situations the significantly different oxygen isotopic compositions of pristine magma and country rock far outweigh small thermal fractionation effects. The final form of the balance becomes:

$$\frac{d\bar{T}_m}{d\bar{T}_a} = \frac{1}{M_m} \left( \bar{C}_a - \bar{C}_m \right) k \bar{M}_a f_a(\bar{T}_a) \frac{d\bar{T}_a}{d\bar{T}_m} \quad (\text{A12})$$

where  $\bar{C}_m$ ,  $\bar{C}_a$  are the traditionally defined normalized deviations from a standard for magma body melt and anatectic melt, respectively. The parameter  $k$  in (A12) defined  $k = C_{a,\text{oxy}}/C_{m,\text{oxy}}$  is the ratio of mass fraction of oxygen in assimilant to that in pristine melt.  $k = 1$  except for rare bulk compositions (e.g., carbonatites and other extremely undersaturated compositions).

## Initial Conditions

Equations A6, A7, A10, A11 and A12 represent a system of differential equations with  $T_m$  as the independent variable. This set of coupled nonlinear ordinary differential equations is of order



$2+t+i+s$  where  $t$  is the number of trace elements,  $i$  is the number of radiogenic isotope ratios and  $s$  is the number of stable isotope ratios in the calculation. For instance, if one models the behavior of Sr, Nd, La, Ba,  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{18}\text{O}/^{16}\text{O}$  in an EC-AFC ‘event’, the number of ODE’s would be 9. These expressions would conserve energy, total mass, mass of Sr, Nd, La, Ba and the isotopic ratios of Sr, Nd, and oxygen during the EC-AFC ‘event’ as melt within the magma body drops from its initial temperature,  $T_m^0$ , to the equilibrium temperature,  $T_{eq}$ .

In order to complete solution of the system of ordinary differential equations, initial conditions must be specified. That is, at  $T_m=T_m^0$ , initial values for  $T_a$ ,  $M_m$ ,  $C_m$ ,  $m$ ,  $a$ ,  $m$  and  $a$  must be chosen. A typical set of initial conditions (in dimensional terms) is as follows: at  $T_m=T_m^0$ , let  $T_a=T_a^0$ ,  $M_m=M_0$ ,  $C_m=C_m^0$ ,  $m=m^0$ ,  $a=a^0$ ,  $m=m^0$  and  $a=a^0$ .

The system of ordinary differential equations is solved numerically by a fourth-order Runge–Kutta method with fixed step size. A coarse step size of 0.001 is suggested as a starting value for exploratory work. Once a set of parameters has been zeroed in on, the step size can be decreased by a factor of two or three until computed variables (e.g.,  $T_a$ ,  $M_m$ ,  $C_m$ ,  $m$ ,  $a$ ,  $a$ ,  $m$ , etc) no longer change with step size. When this limit is reached, the solution may be considered converged and accurate. In general, small step sizes should be used when  $D_a$  or  $D_m$  is very large to guarantee sufficient resolution. A computer program for EC-AFC calculations that runs on virtually any PC or Mac with Excel 98 is available at

<http://magma.geol.ucsb.edu/research/recharge.html>.

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## FIGURE CAPTION

**Fig. 1:** Thermodynamic system approach to RAFC processes. The composite system comprises three subsystems: magma body (melt plus cumulates) of initial mass  $M_o$ , wall rock of mass  $M_a^o$  and replenishment reservoir of mass  $M_r^o$ . The subsystems are separated from their surroundings by rigid, impermeable and adiabatic boundaries throughout the RAFC ‘event’. At the start of RAFC processes, boundaries between all subsystems are made diathermal and permeable, and the composite system relaxes to a state of thermal and chemical equilibrium of maximum entropy. During the RAFC ‘event’, anatectic melt ( $M_a^*$ ) and recharge magma ( $M_r$ ) are added to and homogenized with melt in the standing magma body. Cumulates ( $M_c$ ) form by fractional crystallization and are in isotopic and trace element equilibrium with coexisting melt within the magma body. In the most general RAFC model, the melt portion of the magma subsystem may be broken into several compositionally distinct parts, and a melt extraction efficiency may be introduced so that only a portion of anatectic melt generated is delivered to the magma body. In the more specific model presented in this paper (EC-AFC), melt within the magma body is well mixed, and all anatectic melt generated is added to the magma body. Magma recharge is ‘turned-off’, and the model is referred to as EC-AFC.

**Table 1: Nomenclature**

<b>Symbol</b>	<b>Definition</b>	<b>Units</b>
$T_m^o$	initial magma temperature	K
$T_{l,m}$	magma liquidus temperature	K
$T_{eq}$	equilibration temperature	K
$T_m$	magma temperature	K
$T_{l,a}$	wall rock liquidus temperature	K
$T_a^o$	initial wallrock temperature	K
$h_{fus}$	enthalpy of fusion	J/kg
$h_{cry}$	enthalpy of crystallization	J/kg
$C_{p,m}$	magma isobaric specific heat capacity	J/kg K
$C_{p,a}$	assimilant isobaric specific heat capacity	J/kg K
$T_r^o$	initial recharge magma temperature	K
$T_b$	magma body - country rock boundary temperature	K
$k_a$	thermal conductivity of country rock	W/m K
$k_m$	thermal conductivity of melt	W/m K
$M_r$	mass of recharge magma	kg
$M_c$	mass of cumulates	kg
$M_o$	mass of original magma	kg
$m$	magma expansivity	$K^{-1}$
$f$	fluid expansivity	$K^{-1}$
$K$	permeability	$m^2$
$K_f$	fluid thermal diffusivity	$m^2/s$
$m$	melt thermal diffusivity	$m^2/s$
$l$	melt viscosity	Pa s
$c$	compaction length	m
$*$	matrix viscosity	Pa s
$a$	viscosity of anatectic melt	Pa s
$u$	Darcy velocity	m/s
$g$	gravity	$m^2/s$
$n_o$	fracture number density	$m^{-3}$
$c$	fracture length	m
$d_o$	grain size of porous material	m

$h_{lib}$	heat liberated by cooling and crystallization of magma	J
$h_{abs}$	heat absorbed by heating and partial melting of country rock	J
$M_m$	mass of melt in magma body	kg
$M_a^*$	mass of anatectic melt	kg
$M_a^o$	mass of country rock involved in AFC event	kg
$T_a$	temperature of country rock	K
$H_a$	enthalpy of country rock/anatectic melt partition coefficient for some trace element	J/mol
$H_m$	enthalpy of magma/cumulate partition coefficient for some trace element	J/mol
A	fracture aspect ratio fracture connectivity melt extraction efficiency	
$C_a$	concentration of trace element in country rock <sup>1</sup>	(ppm)
$C_r$	concentration of trace element in recharge magma	(ppm)
$C_m$	initial concentration of trace element in melt	(ppm)
$C_c$	concentration of trace element in cumulates	
$D_a$	$\frac{C_{a,s}}{C_{a,m}}$ bulk solid/melt distribution coefficient between country rock and anatectic melt	
$D_m$	$\frac{C_c}{C_m}$ bulk solid/melt distribution coefficient between cumulates and melt	
$S$	$\frac{C_a^o}{C_m^o}$ ratio of initial concentration of trace element in country rock to initial concentration in melt	
$m$	isotopic ratio in magma	
$r$	isotopic ratio in recharge magma	
$a$	isotopic ratio in assimilant	
$a$	oxygen isotopic composition of assimilant	
$m$	oxygen isotopic composition of magma	
$k_{oxy}$	ratio of mass fraction of oxygen in bulk assimilant and pristine magma	
$f_m(T)$	melt productivity of pristine magma	
$f_h(T)$	melt productivity of wallrock	
R	universal gas constant	8.314 J/mol K

$Rd$	$\frac{g_f KL(T_m^o - T_a^o)}{K_f V_f}$	Darcy Rayleigh number
$Ra$	$\frac{g_m L^3 (T_m^o - T_a^o) \rho_m}{K_m}$	Magma Rayleigh number
$r$	$\frac{M_a^*}{M_c}$	ratio of mass of anatectic melt to mass of cumulates
$B$	$\frac{k_a Rd^{1/2}}{k_m Ra^{1/4}}$	ratio of Darcy to magma chamber Rayleigh number
$\bar{M}_a^o$	$\frac{M_a^o}{M_o}$	non-dimensional mass of assimilant
$\bar{T}_{eq}$	$\frac{T_{eq}}{T_{l,m}}$	non-dimensional equilibration temperature
$\bar{T}_a$	$\frac{T_a}{T_{l,m}}$	non-dimensional assimilant temperature
$\bar{T}_m$	$\frac{T_m}{T_{l,m}}$	non-dimensional magma temperature
$f_m'(\bar{T}_m)$		temperature derivative of magma melt productivity
$f_a'(\bar{T}_a)$		temperature derivative of assimilant melt productivity
$\bar{M}_m$	$\frac{M_m}{M_o}$	non-dimensional melt fraction in magma body
$\bar{C}_a$	$\frac{C_a}{C_a^o}$	non-dimensional concentration of trace element in anatectic melt
$\bar{C}_r$	$\frac{C_r}{C_r^o}$	non-dimensional concentration of trace element in recharge magma
$\bar{C}_m$	$\frac{C_m}{C_m^o}$	non-dimensional concentration of trace element in melt

<sup>1</sup>In text and equations, initial values of trace element concentrations and isotopic ratios denoted by <sup>o</sup>, e.g.,  $c_a^o$  is the initial concentration of trace element in wallrock.

**TABLE 2: Melting temperature, molar and specific enthalpy of fusion and entropy of fusion at  $10^{-4}$  GPa for some silicate and oxide phases**

Phase	Melting Temperature (K)	H <sub>fus</sub> (kJ/mole)	S <sub>fus</sub> (J/mole-K)	h <sub>fus</sub> (kJ/kg)
FeTiO <sub>3</sub>	1640	21.7 ± 0.1	13.2 ± 0.1	143
TiO <sub>2</sub> (rutile)	1870	67.0 ± 0.1	35.8 ± 0.1	838
Fe <sub>2</sub> O <sub>3</sub> (hematite)	1895	114.5 ± 0.2	60.4 ± 0.2	717
Fe <sub>3</sub> O <sub>4</sub> (magnetite)	1870	138.07 ± .05	73.83	596
MgAlO <sub>2</sub>	2408	107 ± 11	44 ± 4	752
Ca <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub>	1750	151. ± 0.5	86.3 ± 0.1	556
Al <sub>2</sub> O <sub>3</sub>	2323	107.5 ± 54	46.3 ± 23	1054
SiO <sub>2</sub> (quartz) <sup>a</sup>	1700	9.40 ± 1.0	5.53 ± 0.56	157
SiO <sub>2</sub> (cristobalite)	1999	8.92 ± 1.0	4.46 ± 0.50	149
MgSiO <sub>3</sub> <sup>a</sup>	1834	73.2 ± 6.0	39.9 ± 3.3	729
CaSiO <sub>3</sub> (wollastonite) <sup>a</sup>	1770	61.7 ± 4.0	34.9 ± 2.3	531
CaSiO <sub>3</sub> (pseudowoll)	1817	57.3 ± 2.9	31.5 ± 1.6	493
CaMgSi <sub>2</sub> O <sub>6</sub>	1665 <sup>b</sup>	137.7 ± 2.4	82.7 ± 1.4	636
Ca <sub>2</sub> MgSi <sub>2</sub> O <sub>7</sub>	1727	123.9 ± 3.2	71.7 ± 1.9	454
Ca <sub>3</sub> MgSi <sub>3</sub> O <sub>8</sub> <sup>b</sup>	1848	125 ± 15	67.5 ± 8.1	350
Fe <sub>2</sub> SiO <sub>4</sub>	1490 <sup>a</sup>	89.3 ± 1.1	59.9 ± 0.7	438
Mn <sub>2</sub> SiO <sub>4</sub>	1620	89. ± 0.5	55.2 ± 0.3	633
Mg <sub>2</sub> SiO <sub>4</sub>	2174	142 ± 14	65.3 ± 6	1010
CaTiSiO <sub>5</sub>	1670	123.8 ± 0.4	74.1 ± 0.2	755
NaAlSi <sub>3</sub> O <sub>8</sub>	1393	64.5 ± 3.0	46.3 ± 2.2	246
NaAlSi <sub>2</sub> O <sub>6</sub> <sup>a</sup>	1100	59.3 ± 3.0	53.9 ± 2.7	293
NaAlSiO <sub>4</sub> <sup>a</sup>	1750	49.0 ± 2.1	28.0 ± 1.2	345
KAlSi <sub>3</sub> O <sub>8</sub> <sup>a</sup>	1473	57.7 ± 4.2	39.2 ± 2.8	207
CaAl <sub>2</sub> SiO <sub>8</sub>	1830	133.0 ± 4.0	72.7 ± 2.2	478
Mg <sub>3</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>12</sub> <sup>a</sup>	1500	243 ± 8	162 ± 5	603
Mg <sub>2</sub> Al <sub>4</sub> Si <sub>5</sub> O <sub>18</sub> <sup>a</sup>	1740	346 ± 10	199 ± 6	591
KMg <sub>3</sub> AlSi <sub>3</sub> O <sub>10</sub> F <sub>2</sub>	1670	308.8 ± 1.3	185 ± 1	733

Adapted from Spera (2000)

<sup>a</sup>Metastable congruent melting

<sup>b</sup>Incongruent melting

**TABLE 3: Partial molar isobaric heat capacity for molten oxide components at 10<sup>-4</sup> GPa**

$C_p$  is approximately independent of temperature at  $T = 1400$  K. Modified from Stebbins et al. (1984) and Spera (2000). The specific isobaric heat capacity for melt can be computed using  $C_p =$

$C_{p_i} W_i$  ( $J K^{-1} kg^{-1}$ ) where  $W_i$  is the mass fraction of the  $i$ th oxide component in the silicate liquid and  $C_{p_i}$  is the specific isobaric heat capacity of the  $i$ th component given in the third column of the table.

Oxide	Molar $C_{p_i}$ (J/gfw K)	Specific $C_{p_i}$ (J/kg K)
SiO <sub>2</sub>	80.0 ± 0.9	1331
TiO <sub>2</sub>	111.8 ± 5.1	1392
Al <sub>2</sub> O <sub>3</sub>	157.6 ± 3.4	1545
Fe <sub>2</sub> O <sub>3</sub>	229.0 ± 18.4	1434
FeO	78.9 ± 4.9	1100
MgO	99.7 ± 7.3	2424
CaO	99.9 ± 7.2	1781
H <sub>2</sub> O <sup>-</sup>	107.0 ± 5.0	5940
Li <sub>2</sub> O	104.8 ± 3.2	3507
Na <sub>2</sub> O	102.3 ± 1.9	1651
K <sub>2</sub> O	97.0 ± 5.1	1030

- Estimated by author.