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THE CONTRIBUTION TO EXOGENIC CO₂ BY CONTACT METAMORPHISM AT CONTINENTAL ARCS: A COUPLED MODEL OF FLUID FLUX AND METAMORPHIC DECARBONATION

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ABSTRACT. Recent work has suggested a possible temporal coincidence between greenhouse intervals and enhanced arc volcanism, motivating the hypothesis that magmatic and metamorphic CO₂ emissions from volcanic arcs, particularly those intersecting crustal carbonates, may play a strong role in modulating the long-term carbon budget of the exogenic system. When hot fluid exsolving from arc magmas interacts with carbonate sequences on active margins, contact metamorphism releases CO₂ to metasomatic fluids that transport carbon to shallow reservoirs. To estimate the magnitude of CO₂ release, here we model how the infiltration of silica-saturated magmatic water into a porous medium facilitates the decarbonation reaction in contact aureoles. Analytical scalings and numerical simulations show that the propagation rate of the reaction front scales with the ratio of the infiltration flux to the mass of the rate-limiting reactant, and accordingly the CO₂ flux increases linearly with the infiltration flux. This simple relationship allows for scaling to predict regional and global scale CO₂ release at continental arcs if magma emplacement rate is known. Using the global rate of continental arc magma emplacement, we estimate that the present-day contact-metamorphic CO₂ release range from ~0.06 to 0.9 Tmol/yr, half-to-one orders of magnitude smaller than the field-based estimates of carbon output in modern arcs (1.5–3.5 Tmol/yr). Yet, the extrapolated CO₂ release from Cretaceous continental arcs via simple infiltration-induced decarbonation is comparable to the release from mid-ocean ridges. CO₂ released from continental arcs amplifies the background flux of CO₂ from direct degassing of the magma, and therefore may have been key in causing the climatic greenhouse interval in the Cretaceous when there was heightened arc activity. Thus, our result supports the hypothesis that global arc flare-ups at continental margins effectively increase CO₂ outgassing coinciding with greenhouse intervals in the geological past. The contribution by arcs to the tectonic CO₂ input could be significant, which needs field-based studies to revise long-term climate models.

Keywords: contact metamorphism, continental arc, reactive transport, long-term climate

INTRODUCTION

An important control on both long-term (> My) and short-term climate is the amount of carbon in the atmosphere. On geologic timescales, carbon in the exogenic system (ocean and atmosphere) is primarily balanced by the inputs from Earth’s interior via magmatic-metamorphic processes and outputs via silicate weathering and biological productivity that sequester carbonate and organic carbon, respectively (Berner and others, 1983; Berner, 1991). Some of these carbonate and organic carbon

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are deposited in the deep ocean, where it eventually finds itself being subducted. A fraction of the subducted carbon returns to the surface or lithosphere (for example, Gorman and others, 2006; Tsuno and others, 2012; Duncan and Dasgupta, 2015; Kelemen and Manning, 2015; Tumiatti and others, 2017); some of it is retained in the slab to be transported to Earth’s deep interior where it may reside for hundreds of millions of years (for example, Dasgupta, 2013; Duncan and Dasgupta, 2017) until being returned to the atmosphere through mid-ocean ridge volcanism or mantle plumes. Carbonate and organic carbon are also deposited as sediments on continental margins, where they can also be stored for hundreds of millions of years. Such carbon can return to the atmosphere by erosion and weathering or during metamorphism and magmatism associated with orogenic processes or volcanism (Lee and others, 2013; Lee and Lackey, 2015; McKenzie and others, 2016; fig. 1A), but their fluxes remain unconstrained (Kerrich and Caldeira, 1998; Lasaga and others, 2001).

Fig. 1. (A) Cartoon of continental arc showing schematic CO₂ degassing on subducting and overriding plates (modified after Lee and Lackey, 2015). (B) A schematic figure showing the geologic conception of this modeling. (C) Model geometrics, and initial and boundary conditions for this simulation. See table 1 for notations.
Many long-term geochemical box models (for example, GEOCARB, Berner, 1991; Berner and Kothavala, 2001) relate tectonic carbon outgassing primarily to the rate of seafloor spreading, with enhanced seafloor spreading resulting in more tectonic degassing at ridges and arcs from the mantle (Berner and others, 1983; Lasaga and others, 1985). It is estimated that about 20 to 40 Teragrams (Tg) of carbon are released as CO₂ from arcs per year globally (Dasgupta and Hirschmann, 2010; Kelemen and Manning, 2015). This estimate carries large uncertainties but is of the same order of magnitude as the carbon inputs from mid-ocean ridges and intra-plate volcanism (13–90 Tg/yr, Dasgupta and Hirschmann, 2010; 8–42 Tg/yr, Kelemen and Manning, 2015).

Recent contributions address decarbonation by regional metamorphism in collisional settings (Groppo and others, 2017; Stewart and Ague, 2018). Challenges remain in quantifying the influence of arc magmas on crustal decarbonation in overriding plates by contact metamorphism, so continental decarbonation is not explicitly accounted for in many global models (for example, Jagoutz and others, 2016). It has been documented that the composition of arc volcanoes intersecting carbonate platforms are featured by high δ¹³C (Mason and others, 2017) and high CO₂/Sₜotal volcanic gas (Aiuppa and others, 2017), indicating that a substantial component of the CO₂ flux from arc volcanoes, particularly continental arcs, derives from crustal carbon in addition to the mantle or subducting slab. Interaction of arc magmas with crustal carbonates on active margins proceeds in two ways: 1) carbonate assimilation in intruding magma, producing calcic melts and CO₂ vapor (Mollo and others, 2010; Dyer and others, 2011; Liao and others, 2013; Carter and Dasgupta, 2015, 2016, 2018; Deegan and others, 2016) and 2) contact metasomatism by infiltration of magmatic fluids into the country rock, producing calc-silicate assemblages and saline COH fluids (for example, Kerrick, 1977; Einaudi and others, 1981; Meinert, 1992; Ferry, 1996; Fulignati and others, 2000). The latter mechanism via fluid-induced metamorphic decarbonation has also been widely considered for continental collision zones (for example, Kerrick and Caldeira, 1998), for which the global flux from continental arcs is estimated in this study.

Compilation of arc lengths over time (Cao and others, 2017) and databases of detrital zircon ages (Condie and Kröner, 2013; Roberts and Spencer, 2015; Paterson and Ducea, 2015; McKenzie and others, 2016) reveal the episodic nature of arc magmatism in the Phanerozoic. The pulses of CO₂ released during periods of vigorous continental arc activity (fig. 1A) potentially contributed to greenhouse intervals (for example, Cretaceous-Paleocene; Lee and others, 2013; Lee and Lackey, 2015; McKenzie and others, 2016). How the CO₂ flux from continental arc magmas scales with the rate of magmatic emplacement is the remaining process that needs to be understood.

In this study, we present a simple model of CO₂ release during contact metamorphism toward an order-of-magnitude estimate of global CO₂ release by carbonate-intersecting magmatism. We apply a self-consistent 1-D finite difference model to an impure marble interacting with silicate-saturated infiltrating fluid. The Darcian flow is modeled with a fixed boundary condition of fluid influx, taking into account reaction kinetics and pore space compaction. We then provide a scaling relationship to relate the steady-state carbon release from contact aureoles to the infiltration fluxes, and globally to the magmatic emplacement rate of continental arcs through time.

**Model Setup**

**Problem Setting**

We use a simple model to approximate natural decarbonation reactions of carbonate minerals with silicates in the country rock and dissolved silicate components, in response to the infiltration of magmatic fluid from a cooling pluton or pegmatitic dike as a fossil fluid channel (fig. 2B; for example, Bowman and other, 1985; Nabelek and Labotka, 1993; Meinert and others, 2003). The goal of this study is
Fig. 2. (A–B) *T*-\(X_{CO_2}\) diagram showing the reaction calcite (Cc) + quartz (Q) = wollastonite (Wo) + CO\(_2\). Reactions with different quartz activities, and at different pressures. (A) The color scales represent Gibbs free energies (\(\Delta G\)) of the reaction. Blue (darker) colors indicate more negative \(\Delta G\), hence a greater driving force for the decarbonation reaction to proceed. At a specific temperature, the devolatilization reaction can be driven by infiltration of water that lowers the activity of CO\(_2\) in the fluid. (C) Metamorphic reactions in the CaO-MgO-SiO\(_2\)-CO\(_2\)-H\(_2\)O model system for comparison.
not to simulate petrogenesis or mineral assemblages of metamorphic calc-silicate or skarn in contact aureoles. Instead, the chemical system is simplified to CaO-SiO$_2$-H$_2$O-CO$_2$ model system (CSHC), in which silicate (quartz or dissolved silica) and carbonate (calcite) phases react to form a calc-silicate phase (wollastonite) and release CO$_2$:

$$\text{SiO}_2 + \text{Calcite} = \text{Wollastonite} + \text{CO}_2 \quad (1)$$

In natural settings, the mineralogy and bulk composition are undoubtedly far more complex, but we have chosen this simplified approach in order to capture first-order behaviors, as a common practice in previous studies (for example, Rice and Ferry, 1982; Balashov and Yardley, 1998). More complicated compositional systems, specific to outcrops and field setting, can be explored in the future as necessary.

When quartz is a stable phase in the assemblage, the fluid is saturated with silica (denoted by $a^*_{\text{qrt}} = 1$). The equilibrium $X_{\text{CO}_2}$ is independent of mineral modes because both reactants are endmembers. The initial molar fraction of CO$_2$ ($X_{\text{CO}_2}$) in the fluid is buffered until one reactant is exhausted (Greenwood, 1975). Lower pressures favor the reaction toward the devolatilization side (fig. 2A). With silica undersaturation, quartz is no longer a stable phase (equivalent $a^*_{\text{qrt}} = 1$) so calcite reacts with the dissolved silica in the fluid. In this scenario, the reaction takes place at higher temperatures or lower $X_{\text{CO}_2}$ (fig. 2A).

The direction of reaction (1) is governed by the change of Gibbs free energy ($\Delta G_j$):

$$\Delta G_j = \Delta G_{j,0} (P,T) + RT \ln a_{\text{CO}_2} - RT \ln a^*_{\text{qrt}} \quad (2)$$

where $\Delta G_{j,0}$ is the change of Gibbs free energy at standard states, $a_{\text{CO}_2}$ is the activity of CO$_2$, and $a^*_{\text{qrt}}$ is the equivalent quartz activity that represents silicate saturation state in the fluid. At constant pressure ($P$) and temperature ($T$), the addition of water dilutes CO$_2$ in the fluid, lowering its activity, leading to negative $\Delta G_j$, and thus driving reaction (1) towards decarbonation (right; fig. 2B; see also Kerrick, 1977; Rumble and others, 1982; Labotka and others, 1988; Heinrich and Gottschalk, 1994; Ferry, 1996; Ferry and others, 2001). Silica undersaturation prevents the reaction from proceeding to the right.

We envision a carbonate sequence in contact with a cooling pluton or a pegmatitic vein that evolves from the pluton, at mid-crustal depth (4 kbar, ~14 km; fig. 1B). Silica-saturated fluid infiltrates laterally, mimicking magmatic devolatilization during the last stage of a magma body’s thermal evolution (fig. 1C). The magmatic fluids react with the country rock, generating a chemical front, which propagates away from the contact with a progressive magmatic fluid influx. The fluid composition at the reaction front is controlled by a balance among the infiltrating fluid, the product of devolatilization reaction, and the consumption and dissolution of silica. The model temperature is kept constant at 650 °C, close to the solidus temperature of hydrous granitic magma. This model explores the relationships between the magmatic fluid influx and the extent of decarbonation to develop a first-order estimate of the carbon flux.

**Governing Equations**

We model isothermal-isobaric fluid flow in a porous medium (eq 3), coupled with reaction kinetics and dynamic pore space generation/compaction (see below). The devolatilization reaction leads to changes in the amount and composition of fluid present in the pore space (eq 4), which also depends on fluid advection and diffusive transport of chemical components (CO$_2$ and SiO$_2$ in this case; eq 5).

$$\phi \nu_j = - \frac{k_b}{\mu_j} \cdot \frac{\delta P_j}{\delta x} = \frac{k_b}{\mu_j} \cdot \frac{\delta P_j}{\delta x} \quad (3)$$
The symbols are defined in Table 1. Equation (3) is Darcy’s Law, in which \( \phi \nu_j \) is the fluid flux (\( m^3 \) fluid \( m^{-2} \) rock yr\(^{-1} \)), also known as the “Darcy velocity” \( (v_D) \). \( P_c = P_l - P_f \) is
the effective pressure, which means the deviation of fluid pressure ($P_f$) from lithostatic ($P_l$), and is of special significance in the evolution of porosity (see below).

Equations (4) and (5) describe mass conservations of fluid and solute (CO$_2$ or dissolved silica), respectively. $R_i$ in equations (4) and (5) is the production rate of CO$_2$ (positive) or consumption rate of silica (negative). The unit of production or consumption rate is mole per second per m$^3$ of bulk rock; here $j = 1$ is the only reaction (reaction 1), $v_j = 1$ is the stoichiometric coefficient, and $M_j = 0.044$ is the molecular weight of CO$_2$. The right-hand side of equation (5) accounts for advection, hydrodynamic dispersion and chemical reaction. $D_{HD}$ is the hydrodynamic dispersion coefficient. Equation (5) is an approximate permeability-porosity relationship (Brace and others, 1968). The bulk fluid density is a function of the CO$_2$ concentration in the H$_2$O-CO$_2$ binary fluid and is calculated using the equation of state of Holland and Powell (2003).

The equations are solved using numerical methods in a finite-difference scheme. In dealing with equation (6), an operator-splitting method is adopted: Crank-Nicolson scheme for the diffusion term and Barton’s scheme (Centrella and Wilson, 1984) for the advection term.

**Reaction Kinetics**

The rate of reaction progress, $R_p$, is given by Lasaga (1986) and Lasaga and Rye (1993):

$$R_j = \kappa_j v_j A_j |\Delta G_j|^{n_j}$$

in which $v_j$ is the stoichiometric coefficient of the product. $G_j$ is the change of Gibbs free energy (eq 2); the more fluid $X_{CO_2}$ (and its activity $a_{CO_2}$) deviates from equilibrium, the more negative $\Delta G_j$ is, and thus the faster decarbonation takes place (fig 2). On the other hand, silica undersaturation slows down or prevents the reaction. $A_j$ is the reactive surface of rate-limiting minerals. In this study, we use a representative surface area of 100 m$^2$ m$^{-3}$ (Ague and Rye, 1999) for 10 volume percent quartz, corresponding to spherical quartz grain of ~3 mm. Previous studies document surface-control reaction rates (for examples, Steefel and Lasaga, 1994) as well as more complex behaviors (Dohmen and Chakraborty, 2003). For simplicity, $A_j$ decreases linearly as the reactants are being consumed in this model.

$\kappa_j$ is the intrinsic reaction rate constant that follows an Arrhenius relationship:

$$\kappa_j = \kappa_{j,0} \exp \left[ -\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right]$$

where $\kappa_{j,0}$ is the intrinsic reaction rate at a reference temperature ($T_0$), $E_a$ is the activation energy, and $R$ is gas constant. The kinetic law for most specific decarbonation reactions remains to be investigated. Lasaga and Rye obtained a linear kinetic law ($n_j = 1$) by fitting the experimental data for muscovite dehydration of Schramke and others (1987). Assuming that the calibration of Lasaga and Rye (1993) is broadly applicable to metamorphic reactions, it has been used to quantitatively assess the reaction rates between silicates and carbonates in various modeling studies (for example, Ague, 1998, 2000; Balashov and Yardley, 1998; Lüttge and others, 2004; Nabelek, 2009; Tian and Ague, 2014). Future experiments will need to calibrate the reaction rates involving quartz, calcite, and COH fluid, but it is shown below that the first-order results of this study are largely insensitive to the kinetic laws selected.

**Porosity Evolution**

Rock permeability controls fluid flow and thus reaction progress. The generation of porosity enhances permeability and increases the influx of magmatic fluids. For the
representative reaction (1), the solid volume of wollastonite is about 1/3 smaller than reactants quartz + calcite, but is larger than calcite (Holland and Powell, 1998). The rate of porosity generation scales with \(-v_i R \Delta V_s\) in which \(\Delta V_s\) is the change in solid volume across the reaction (m³ mol⁻¹).

The reaction between quartz and calcite enhances the porosity of the medium, leading to positive feedback between reaction and fluid flow (for example, Rumble and others, 1982; Baumgartner and Ferry, 1991). After quartz is exhausted the reaction with dissolved silica transforms calcite to wollastonite of larger molar volume, so the expansion of solid volume clogs the generated pore space.

Porosity can be decreased by plastic creep if the fluid pore pressure \(P_f\) is lower than lithostatic \(P_l\) (Zhang and others, 1990). The effects of reaction and compaction are combined as:

\[
\frac{\delta \phi}{\delta t} = -\phi_{cr} - v_i R_i \Delta V_s
\]

where \(\phi_{cr}\) is the porosity loss due to plastic deformation (s⁻¹). The general expression of compaction rate is (Walker and others, 1990):

\[
\phi_{cr} = A(\phi) \exp(-H_{cr}/RT) P_e d_g^m
\]

where \(H_{cr}\) is the energy of activation, \(P_e\) is the effective pressure (=\(P_l - P_i\)), and \(d_g\) is grain size. The power-law rate expressions of marble are derived from experiments (for example, Walker and others, 1990; Zhang and others, 1994; Paterson, 1995). A deformation mechanism map is provided in Balashov and Yardley (1998). For fluid underpressure by a few MPa, the predominant deformation mechanism is pressure solution, and the compaction rate \(\phi_{cr}\) is proportional to \(P_e\) (Paterson, 1995; Zaraisky and Balashov, 1995). Grain boundary sliding provides a limiting rate for low porosity (<1 %, Walker and others, 1990). Because the deformation mechanisms are positively correlated to the porosity, the porosity reaches a steady state at the reaction front (see below).

**Initial and Boundary Conditions**

The default initial and boundary conditions are summarized in figure 1C, for a protolith assemblage of 90 vol.% calcite + 10 vol.% quartz. The dependence of modeling results on the quartz mode is then discussed. The initial fluid \(X_{CO_2}\) is set to be in equilibrium according to reaction (1) at the model temperature and pressure. The infiltrating fluid from the pluton is assumed to be (1) pure water (for example, Ferry, 1996) or (2) aqueous fluid that is silica saturated. The far-field fluid composition gradient within the country rock is zero. The silica content is calculated using the calibration of Manning (1994), and we assume that the activity of silica follows Henry’s Law in this dilute solution.

The initial country-rock porosity is assumed to be 1 percent. Because porosity is generated by the reaction and reaches a steady-state at the reaction front, the initial porosity has no significant impact on the model results.

Above the brittle-ductile transition zone, the rigid rock matrix supports a pore network through which fluid percolates, so the vertical fluid pressure gradient approaches hydrostatic pressure. The fluid exsolving from the viscous magma is assumed to be under lithostatic pressure, which is greater than the hydrostatic pressure in the country rock. Thus, the contrast between the two pressure regimes results in a pressure gradient that drives fluid flow into the country rock.

At 14 km near the brittle-ductile transition zone, the difference between lithostatic and hydrostatic is about 2.5 kbar, and the permeability is about \(2 \times 10^{-18} \text{ m}^2\) (Manning and Ingebritsen, 1999). The fluid flux originating from a pluton of 10 km
radius would thus be approximately $0.014 \text{ m yr}^{-1}$ (fig. 3), the highest in the vertical section. In this model, the fluid flux from the pluton is imposed as a boundary condition; the front propagation rate and CO$_2$ release are functions of this boundary condition. In the default setting, the fluid flux from the contact is set $v_D = 0.01 \text{ m yr}^{-1}$ that does not vary with time, corresponding to the fluid velocity $v_f = 1 \text{ m yr}^{-1}$ with an initial 1 percent porosity ($v_p = v_f \cdot \phi$). The fluid pressure boundary condition at the contact is set as lithostatic ($P_{e,L} = 0$), and the pressure gradient is governed by Darcy’s Law (eq 2) and the fluid flux inside the modeled space.

Remarks on Model Assumptions and Simplifications

In this isothermal-isobaric simulation, we adopt the highest pressure (4 kbar) in the brittle upper crust which corresponds to the brittle-ductile transitional depth, and the lowest temperature (650 °C) of the intrusive magma which approaches the solidus temperature of granitoid. Decarbonation reaction accelerates with rising temperature and decreasing pressure (fig. 2A), so higher temperatures of the cooling pluton and shallower depth favor greater CO$_2$ release. Surface carbonate can be transported to lower-crustal depth by under-thrusting (for example, DeCelles and others 2009; fig. 1A), where decarbonation is documented by deep-seated contact aureoles (Ague and Brimhall, 1988; Pickett and Saleeby, 1993; Ji and others, 2014) and high-pressure skarn minerals (see Lee and others, 2013 for a summary of scheelite occurrences in Cordillera). The pressure gradient between lithostatic and hydrostatic at this depth leads to large infiltration flux, so that the chemical front propagates fast in the simulation. It is shown below that the front propagation and decarbonation rates scale with the infiltration flux; however, the steady-state estimate of global decarbonation in

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**Fig. 3.** Depth-profiles of (A) lithostatic and hydrostatic pressures, (B) pressure difference, (C) permeability (Manning and Ingebritsen, 1999) and (D) fluid flux from a cooling pluton of 10 km radius.
the general conclusion is largely on the basis of mass balance and is independent on specific infiltration fluxes.

The model dimension (30 m) corresponds to a conduction timescale of 27 years, much shorter than the modeled duration of a thousand years. The reaction rate is low, so the endothermic effect of reaction \((\Delta H \approx 90 \text{ kJ mol}^{-1})\) causes minor temperature gradient over the length scale of reaction front \((L \approx 2 \text{ m})\) considering conduction only:

\[
\Delta T \approx -\left(\frac{\Delta H \cdot R}{k/L^2}\right) \approx 0.3 \degree C
\]

where \(k \approx 1 \text{ W m}^{-1} \text{ K}^{-1}\) is the thermal conductivity of marble. The small temperature gradient is further smeared by heat advection. Thus, the system approaches isothermal, as is simplified, within the modeled spatial and temporal dimensions.

The devolatilization of metacarbonate-rich rocks in shallow contact metamorphism has been widely studied. The magmatic fluids react with country rocks both at pluton contacts and along the flow pathways that manifest as various vein selvage systems. The near-hydrostatic fluid pressure regime allows convection (for example, Cathles, 1977; Norton and Knight, 1977; Hanson, 1995; Cui and others, 2001); hence percolating meteoric water and groundwater heated by the pluton also play a role in metasomatic processes (for example, Einaudi and others, 1981; Guy and others, 1988; Meinert, 1997; Dubinin and others, 2011; D’Errico and others, 2012; Ramos and others, 2018). For example, more realistic and sophisticated models include fluid flow in response to intrusion-induced thermal convection, production of fluids during magma crystallization, and fluid thermal expansion (for example, Hanson, 1995). The maximum fluid flux at the pluton-country rock contact for this type of model is \(1-5 \times 10^{-7} \text{ kg m}^{-2} \text{ s}^{-1}\) or \(0.003-0.015 \text{ m}^3 \text{ m}^{-2} \text{ yr}^{-1}\), close to the boundary condition of fluid flux used in this model \((0.01 \text{ m yr}^{-1})\). Our study explicitly considers the primary magmatic water that makes up only a fraction of infiltration flux, but meteoric and hydrothermal fluxes expand the extent of decarbonation.

Natural systems are beyond simplified CSHC model system, and the reactions lead to the formation of calc-silicate skarns (Kerrick, 1977; Meinert, 1987; Kwak, 1986; Spooner, 1993; Baker and others, 2004). For example, the addition of MgO to the model system includes dolomite as a reactant, and gives rise to magnesium-silicate products like forsterite, diopside, tremolite, and talc (fig. 2C). Thus calc-silicate rocks in natural contact aureoles are characterized by talc, tremolite, diopside and forsterite isograds, and pure wollastonite marble is not common. Similarly, if \(\text{Al}_2\text{O}_3\) is included, the typical decarbonation reaction is grossular-forming. We note that the decarbonation reactions are topologically similar in the \(T-X_{\text{CO}_2}\) space, and a large number of reactions take place at temperatures lower than reaction (1), so decarbonation in a chemically more complex system would be greater than in the model system. We use the simplest possible reaction to explore the first-order relationship between fluid infiltration and decarbonation, which also apply to other reactions. The reactions producing talc and tremolite, for instance, would produce qualitatively similar \(\text{CO}_2\) flux at 470 °C as modeled in this study (fig. 2C).

In 2-D or 3-D cases, layer-parallel flow also introduces silica-saturated fluid from adjacent schists by diffusion and dispersion that triggers decarbonation at the lithologic contacts (Yardley and Lloyd, 1995; Ague, 2000). The structural settings like beddings and faults are considered the principal control of fluid flow direction (Ferry and others, 1998, 2002), so the fluid does not necessarily flow perpendicular to the pluton-country rock contact.

\(\text{CO}_2\) in fluids would also derive from carbonate dissolution (for example, Caciagli and Manning, 2003), which is an additional source of \(\text{CO}_2\). Dissolution of carbonate at 650 °C, 4 kbar is about 0.0033 molal in pure water (Caciagli and Manning, 2003),
which is orders of magnitude smaller than the $X_{\text{CO}_2}$ buffered by the decarbonation reaction. Carbonate dissolution could be significantly enhanced by interaction with silicates (Tumiati and others, 2017) and fluid salinity (Newton and Manning, 2002), as a consequence of complexing and decrease in water activity.

**Scaling Analysis**

In this model of reactive transport, the fluid composition is specified by not only the mineral–fluid equilibrium but also a rapidly attained, kinetically controlled steady state during infiltration-driven metamorphic reactions (Lasaga and others, 2000). To reveal space-time relations and the general characteristics of the process (Lichtner, 1993), we now develop scaling relationships with assumptions, a simplified version of derivation presented in Ferry and others (1991) and Dipple and Ferry (1992), before we delve into numerical results.

For systems in which advection dominates, that is, for large Péclet number ($L \times v_f / D_{HD} = 130$), the diffusion term can be neglected in equation (5), such that

$$\frac{\delta \phi C_s}{\delta t} = -\frac{\delta (v_f \phi C_s)}{\delta x} + R_j$$  \hspace{1cm} (11)

Equation (11) can be simplified and rearranged, and assuming that $v_f$ is constant, yields

$$\frac{\delta \phi C_s}{\delta t} + v_{\text{front}} \phi C_s = - (v_f - v_{\text{front}}) \frac{\delta \phi C_s}{\delta x} + R_j$$  \hspace{1cm} (12)

in which $v_{\text{front}}$ is the rate of front advancement. The left-hand side is the material derivative of $\phi C_s$, which is zero at steady state. On the right-hand side, the fluid velocity is greater than the front advancement rate ($v_{\text{front}}$) by orders of magnitude. Thus, neglecting spatial variations of porosity, equation (12) simplifies to:

$$R_j = v_f \phi \frac{\delta C_s}{\delta x}$$  \hspace{1cm} (13)

According to the linear reaction kinetics of equation (7) and the expression of $\Delta G$ in equation (2), the reaction rate can be approximated as:

$$R_j = -k' \ln \left(\frac{C_s}{C_{eq}}\right) = -k' \ln \epsilon$$  \hspace{1cm} (14)

in which the $k'$ constant (mol m$^{-2}$ s$^{-1}$; $k' > 0$) involves the intrinsic reaction rate constant, rate-limiting surface area, temperature, activity coefficient, and molar volume of fluid; $\epsilon = C_s / C_{eq}$ is a normalized concentration ($\epsilon < 1$) and $\epsilon = 1$ represents fluid in equilibrium so $R_j = 0$.

For advection-dominated reactive transport, the degree of local equilibrium can be characterized by the Damköhler number (Boucher and Alves, 1959):

$$Da = k' L / v_f$$  \hspace{1cm} (15)

The Damköhler number is a dimensionless ratio of the relative time scale of advection ($L / v_f$) over the time scale of chemical equilibration ($1 / k'$). The larger the Damköhler number is, the more closely the fluid composition approaches local chemical equilibrium, and the more closely the chemical profile of the fluid resemble a step function. In this model, the Damköhler number is fairly large, and local equilibrium is also demonstrated by sharp wollastonite isograds in the field (for example, Ferry and others, 2001). However, as the advancement of the front critically depends on the
exhaustion of one of the reactants, it is worth comparing the relative timescales of transport and exhaustion.

We first substitute $R$ (eq 14) into the simplified transport-reaction equation (eq 13):

$$ \nu D \frac{dc}{dx} = -k' \ln c \tag{16} $$

According to mass balance, the carbon flux can be approximated as the product of the rate of front advancement and total carbon liberated per unit length. The latter is equivalent to the amount of rate-limiting reactant by stoichiometry when the reaction front swipes across. We then rearrange equation 16 and apply mass balance:

$$ C_{\text{react}} v_{\text{front}} = \int_0^\infty Rdx = -k' \int_0^\infty \ln c \ dx = \nu D C_{\text{eq}} \tag{17} $$

in which $C_{\text{react}}$ is the concentration of rate-limiting reactant in the solid assemblage (mol m$^{-3}$). The flux of carbon release is a function of only the infiltration flux at a specific $P$-$T$ condition, and the front propagation rate yields a linear relationship with the fluid flux:

$$ v_{\text{front}} = \nu D (C_{\text{eq}} / C_{\text{react}}) \tag{18} $$

Thus, time-integrated flux could be indicated by the reaction front distance (see also Ferry and others, 2001). Strictly, $\nu D$ and $\phi$ are functions of the distance from the contact ($x$), even in steady state (see below). As is also suggested by systematic variations of fluid $\delta^{18}O$ and $X(\text{CO}_2)$ away from the contact (for example, Bowman and others, 1985), the fluid flux ahead of the reaction front is a sum of infiltration flux and CO$_2$ production at the front. In addition, the kinetic constant $k'$ is not a constant because the surface area decreases as reactants are being consumed and the molar volume of the fluid varies with the fluid composition. We also note that the simplification applies when the mode of quartz is large enough so that the propagation rate of exhaustion front is negligible with respect to the fluid velocity.

### RESULTS OF NUMERICAL SIMULATIONS

The simulation results, without and with dissolved silica in the simulations, are presented in figure 4, in which the fluid composition (figs. 4A, 4F, and 4G), porosity (figs. 4B and 4H), fluid flux (figs. 4C and 4I), reaction rate (figs. 4D and 4J), and the mineral modes (figs. 4E and 4K) are shown as a function of distance in the direction of fluid flow at discrete times. The protolith contains 10 volume percent quartz and 90 volume percent calcite, with an infiltration flux 0.01 m yr$^{-1}$.

Three regimes are identified along the profiles: exhausted reactant, reaction front, and unreacted reactant (figs. 4E and 4K). The chemical gradient of the fluid is greatest at the reaction front (figs. 4A, 4F, and 4G). Ahead of the reaction front, the fluid composition is buffered by quartz + calcite and approaches equilibrium with the assemblage. Behind the reaction front, the reactant quartz has been exhausted. If silica dissolution is not incorporated, the fluid composition is imposed by the external infiltration (fig. 4A); with silica dissolution incorporated, the fluid $X_{\text{CO}_2}$ and $a_{\text{gr}}$ reach a steady state (figs. 4F and 4G). In the latter case, the silica content in the fluid is minimal so that the steady state is reached almost instantaneously when such fluid reacts with the assemblage. The fluid flux is constant ahead of and behind the reaction front due to mass conservation; devolatilization taking place at the reaction front adds CO$_2$ to the fluid flux (fig. 4C).
As wollastonite forms at the expense of quartz and calcite (fig. 4E), the porosity increases significantly. The porosity is subsequently reduced by plastic deformation. Therefore, the advancement of the front, with compaction included, slightly lags the non-compaction scenario (fig. 4B). In reality, the transient porosity facilitates fluid flow, but the increased permeability cannot sustain the hydraulic head. Accordingly, a local pressure gradient caused by permeability contrast induces fluid flow normal to the propagation direction (Yardley and Lloyd, 1995). 2-D simulation is needed to reproduce the reaction-generated sink of pore fluid, but qualitatively, additional fluid flux from the 2nd or 3rd dimension enhance local decarbonation.

In cases where calcite is transformed to wollastonite by reaction with dissolved silica (fig. 4K), the solid volume expansion destroys pore spaces (fig. 4H). Decarbonation reaction still proceeds despite the exhaustion of quartz (fig. 4J), but at a slower pace. The local pressure gradient causes fluid flow normal to the propagation direction (fig. 4G). The effects of pore space compaction are shown in part B.

Fig. 4. Modeling results showing plots of fluid composition (A, F, G), porosity (B, H), fluid flux (C, I), reaction rate (D, J), and changes in mineral modes (E, K) across the advancing reaction front at different times, for an infiltrating flux 0.01 m yr\(^{-1}\) from the pluton. The left panels display simulation results without dissolved silicate, and the right panels with dissolved silica in the model. The effects of pore space compaction are shown in part B.

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rate due to silica undersaturation (eq 2). Thus, slightly greater decarbonation takes place when silica dissolution is included (figs. 4E and 4K). In natural settings, a metasomatic rind of dense calcsilicate could act as an impermeable barrier that prevents further fluid infiltration and forces fluid channeling (for example, Harley and Santosh, 1995; Cartwright and Buick, 1995; Skelton and others, 2000). For example, anomalies of geochemical tracers do not penetrate deeper than a few centimeters into the Valentine wollastonite deposit, New York (Gerdes and Valley, 1994). In addition, reaction-induced overpressure could also cause local fluid backflow (for example, Balashov and Yardley, 1998).

The model duration is 1,000 yr, of the same order of magnitude as local metasomatism by fluid infiltration events (for example, Palin, ms, 1992; van Haren and others, 1996; Skelton, 2011), producing a contact metasomatic zone of a few meters in width which is typical for metasomatic selvages. Natural metasomatic zones could be a cumulative product of multiple pulses of fluid infiltration (for example, Jamtveit and others, 1993; Skelton and others, 2002; Ayers and others, 2006; Ramos, ms, 2017).

The reaction front advances at a constant rate that is a function of the flux of infiltration from the contact and the rate-limiting surfaces (denoted by the amount of reactant in this case) and is further illustrated in figure 5. As the scaling analysis predicts, the distance of advancement yields a nearly linear relationship with the duration, especially after the first couple of hundreds of years when the front propagation reaches a quasi-steady state with reference to the fluid. With the infiltration flux boundary condition \( v_D = 0.01 \text{ m yr}^{-1} \), the front advances 6 meters from the contact in about 870 years, at a steady-state rate about 6.9 mm yr\(^{-1}\), significantly slower than the pore fluid velocity (1 m/yr) (fig. 5A). At 650 °C and 4 kbar, the equilibrium \( X_{CO_2} \) is 0.092, corresponding to \( C_{eq} = 3.3 \times 10^5 \text{ mol m}^{-3} \). 10 volume percent quartz corresponds to \( C_{react} = 2.2 \times 10^3 \text{ mol m}^{-3} \). Thus, the reaction front propagates at 6.7 mm yr\(^{-1}\) with the infiltration flux 0.01 m yr\(^{-1}\), very close to the advancement rate from the numerical model (6.9 mm yr\(^{-1}\); fig. 5A). The incorporation of dissolved silica
slightly slows down the propagation rate (purple curve in fig. 5A), likely due to a fluid supply of higher $X_{\text{CO}_2}$ to the reaction front (fig. 4F) and thus slower reaction rate at the front (fig. 4J).

Compaction slightly slows propagation of the exhaustion front in the first 200 years with respect to the non-compaction case. Otherwise, the non-compaction propagation curve (blue in fig. 5A) is parallel to the compaction case, so the steady-state rates for both cases are almost identical.

The rate at which the reaction front advances is positively correlated with the infiltration flux. If the infiltration flux from the contact is doubled or halved, the steady-state propagation rate is sub-quantitatively doubled or halved, consistent with the scalings (fig. 5A). The propagation rates switch in response to the change of infiltration flux boundary value—the red curve in figure 5A is parallel to the $v_{D,L} = 0.005 \text{ m/yr}$ curve from 400 yr when the infiltration flux is halved.

The advance rate is also a function of the modes of reactants, since the reaction front does not advance until one reactant is exhausted. The reaction front propagation rate approaches the fluid velocity if one reactant is infinitesimal, being exhausted quickly and eliminating any reactive transport. Front propagation is slowest when reaction products are subequal in proportion, that is, quartz: calcite = 50:50 (in mole%). When the mode of quartz (vol.%) is doubled or halved in the protolith assemblage, the advance of the front is proportionally accelerated or retarded, respectively (fig. 5B). The front advancement is decreased when it propagates across a lithologic contrast of quartz mode variation (10 vol.% → 20 vol.%; green curve and inset in fig. 5B). The section segment is parallel to the curve of 20 volume percent quartz case.

The carbon flux ($\text{mol m}^{-2} \text{ yr}^{-1}$) is a product of the fluid flux ($\text{m yr}^{-1}$) and the carbon content in the fluid ($\text{mol m}^{-3}$). Because the far-field fluid composition in the country rock is internally buffered, CO$_2$ emission from the modeled section is directly correlated with the fluid flux. For a fluid infiltration flux of 0.01 m yr$^{-1}$ at the contact, 38 moles of CO$_2$ are liberated per square meter contact area per year (fig. 6A). Incorporation of silica dissolution slightly enhances carbon emission (purple curve in fig. 6A), but the difference is negligible. Note that the numerical solution becomes less
stable when one more diffusion-advection equation is included. When the infiltration flux is doubled or halved, the steady-state carbon flux is approximately doubled or halved (fig. 6A). On the other hand, the carbon flux from the aureole is largely insensitive to the variation of quartz mode (fig. 6B). The system reaches a steady state sooner with a smaller quartz mode (fig. 6B).

In summary, our simulations indicate that 1) the pore fluid composition and mineral modes reach quasi-steady state profiles in 100~200 years; 2) the steady-state advancement rate of the reaction front approximately yields linear relationships with the infiltration flux and the amount of rate-limiting reactant; and 3) the carbon flux is also a linear function of the infiltration flux, but is insensitive to the amount of the rate-limiting reactant.

**Discussion**

**Decarbonation by Contact Metamorphism on a Global Scale**

It is shown above in a simplified physical picture that the first-order approximation of front advancement rate is a linear function of the infiltration flux and the amount of rate-limiting reactant, which does not involve the specific kinetic law or the rock rheology. Accordingly, the carbon flux from contact aureoles simply scales with \( v_D \times C_{eq} \) and is independent of the properties of the country rock. In this section, we discuss the potential contributions to global CO\(_2\) outgassing by contact metamorphism.

Decarbonation in a contact aureole is driven by the infiltration of magmatic fluid from the cooling pluton into the country rock. A first-order approximation suggests that the steady-state carbon flux depends on the infiltration flux and is insensitive to the protolith assemblage (quartz/calcite ratio), initial porosity, reaction kinetics, rock rheology, et cetera. For a series of plutons emplaced into carbonate-bearing country rock, the total carbon release (\( M_C, \text{mol} \)) can be calculated as:

\[
M_C = \sum_i J_{C,i} A_i = \sum_i (k F_{inf,i}) A_i = k \sum_i F_{inf,i} A_i = k V_{inf}
\]

where \( J_{C,i} \) is the steady-state flux of carbon from the \( i \)-th aureole, \( A_i \) is the representative contact surface area of the \( i \)-th pluton, \( F_{inf,i} \) is the steady state infiltrating flux of magmatic fluid (m yr\(^{-1}\)), \( k \) is a scaling factor (\( J_{C,i} = k \cdot F_{inf,i} \)); according to the scaling and simulation, 38 mol m\(^{-2}\) yr\(^{-1}\) CO\(_2\) flux is generated in response to infiltration flux 0.01 m yr\(^{-1}\), thus \( k = 3.8 \times 10^5 \text{ mol m}^{-3} \). \( V_{inf} \) is the total volume of infiltrating magmatic fluid per unit time. Thus, the total carbon release scales with the total volume of fluid infiltration. Once we establish that the flux of infiltrating magmatic fluid at continental arcs is a function of the emplacement rate of granitoid magma, the global carbon release from the contact aureoles can be estimated.

Estimates of the global magmatic emplacement rate in continental arcs carry large uncertainties. Crisp (1984) compiled volumetric rates of magma emplacement and volcanic output for durations of igneous activity greater than 300 yr, and estimated the global magma emplacement rate over the last 180 Myr. However, most data of subduction-zone arc magmatism in this compilation are from recent (<10 Ma) or active magmatic systems. Thus, we take this estimate as a representative of the present-day magmatic emplacement rate. The estimate for subduction zone-related volcanism ranges between 0.4 km\(^3\) yr\(^{-1}\) and 0.6 km\(^3\) yr\(^{-1}\), and plutonism between 2.5 km\(^3\) yr\(^{-1}\) and 8 km\(^3\) yr\(^{-1}\). The estimate of Crisp (1984) is relatively conservative compared with other estimates (Nakamura, 1974: volcanism: 0.75 km\(^3\) yr\(^{-1}\); Fujii, 1975: volcanism: 1.1 km\(^3\) yr\(^{-1}\), plutonism: 15.2 km\(^3\) yr\(^{-1}\). About 50 to 60 percent of subduction zone magmatism takes place in continental arcs (Crisp, 1984). Subduction-zone magmas typically contain about 4 to 5 weight percent water (for example,
Wallace, 2005; Plank and others, 2013), most of which exsolves during magma crystallization and cooling, corresponding to ~10 to 12 volume percent of water in the magmas.

We assume that 10 percent to 40 percent of continental arc granitoid magma intrudes carbonate-bearing rocks. Although limestone and dolostone constitute ~10 to 15 percent of all sedimentary rocks (Blatt and others, 2006), they are concentrated on continental shelves and slopes where most marine carbonate accumulation takes place. For example, the Gangdese Batholith intruded the southern margin of Lhasa Terrane in response to the Mesozoic-early Cenozoic northward subduction of the Neo-Tethyan Plate (fig. 7; for example, Ji and others, 2014). The major carbonate formations of the Jurassic-Cretaceous passive-margin sequence are shown in figure 7A. The direct contact of these rocks with Cretaceous plutons measures 0.6 × 10^3 km, out of a total 2.5 × 10^3 km contours of the plutons. We note that other formations, clastic and volcano-sedimentary units not depicted in figure 7A, all contain limestone layers that could be locally dominant. The carbonate rocks are not favored in terms of preservation, so its proportion from the geologic map is a conservative estimate. In another instance, the Sierra Nevada Batholith was built on thick Proterozoic to Paleozoic continental-margin sediments; in some regions, limestones and dolostones account ≥50 percent of the sequence (Stevens and Greene, 1999). Most sedimentary or weathered volcanic rocks contain a certain amount of carbonate minerals and infiltration-driven decarbonation could affect other carbonate-bearing lithologic units (for example, Ferry, 1984, 1988). The decarbonation reaction in this model, based on which the carbon flux is estimated, is far from completion, in agreement with field-based observations.

Thus, the model estimate of global carbon release via contact metamorphism at continental arcs is 0.06–0.9 Tmol yr^{-1} (fig. 8A). This estimate critically depends on the proportion of carbonate country rocks which the continental-arc plutons intrude, but the order-of-magnitude estimate remains the same with a reasonable assumption of country-rock lithology (fig. 8B). This value is about half-to-one orders of magnitude smaller than the estimates of CO₂ outgassing through arc volcanism (1.5–3.5 Tmol yr^{-1}, both island and continental arcs; fig. 8A; Sano and Williams, 1996; Marty and Tolstikhin, 1998; Hilton and others, 2002; Dasgupta and Hirschmann, 2010; Kelemen and Manning, 2015). However, in these previous estimates of CO₂ outgassing at arcs, carbon is thought to be largely or entirely mantle-derived.

We model the metasomatic endmember of magma-carbonate interaction; shallower, cooler, and more silicic intrusion favors decarbonation by contact metamorphism (Einaudi and others, 1981; Meinert, 1992). Alternatively, assimilation of crustal carbonate, the magmatic endmember, is facilitated by the intrusion of hotter, deeper, and more primary magma (Carter and Dasgupta, 2016). Substantial carbonate assimilation manifests in active volcanic systems (Barnes and others, 2005; Chadwick and others, 2007; Troll and others, 2012), petrologic experiments (Mollo and others, 2010; Carter and Dasgupta, 2015, 2016, 2018), and residual calc-silicate xenoliths in magma (Gaeta and others, 2009; Dyer and others, 2011; Shen and others, 2013). The capacity of CO₂ incorporated by assimilation could be one or two orders of magnitude greater than the present-day global arc volcanic CO₂ flux (Carter and Dasgupta, 2016), especially if the carbonate strata of interest is dolostone-rich than limestone-rich (for example, Carter and Dasgupta, 2018). If the emplaced magma at continental arcs, which interacts with carbonate, assimilates 10 percent carbonate wall rocks (for example, 14–15% at Vesuvius, Iacono-Marziano and others, 2009; 10% at Merapi, Chadwick and others, 2007; 7% at Calli Albani, Gaeta and others, 2009), cumulative 0.3–5 Tmol/yr CO₂ is released (fig. 8A). The CO₂ release from assimilation depends on the intruding magma (Carter and Dasgupta, 2016).
Fig. 7. (A) A simplified geologic map of South Lhasa Terrane from longitude 90°E to 92.5°E, showing the distribution of plutons and Jurassic-Cretaceous carbonate sequences (modified from 1:250,000 scale maps from the PR China Geologic Maps: Lhasa District, H46C003001 and Zetang Town District, H46C003002; Tibet Geological Survey, 2006a, 2006b). (B) A schematic geologic map of southern Tibetan plateau showing the Gangdese Batholith along the southern edge of the Lhasa terrane. (C) Distribution of continental arcs on the paleomap of Cretaceous (90 Ma). The purple curve represents Gangdese Batholith (Gd). Modified from Cao and others, 2017.
and is largely uncertain, but is significant in the total CO$_2$ release from arcs. The estimate is largely consistent with the previous estimate for modern arcs (fig. 8A) and serves as a test for the assumptions. This portion of the CO$_2$ release is not included in the discussion of the next section.

Contributions of Contact Metamorphism to Long-Term Carbon Budget

In the Phanerozoic, major greenhouse intervals occurred in Cambrian-Ordovician, Devonian-Carboniferous, and Cretaceous-Paleocene (for example, Berner and Kothavala, 2001; Park and Royer, 2011), which largely match the periods of enhanced continental arc activities as are indicated by the global length of arcs (fig. 9A; Cao and others, 2017) and cumulative frequencies of young detrital zircon (fig. 9A; McKenzie and others, 2014, 2016). Arc magmatism and associated metamorphism along active continental margins are considered to be a significant CO$_2$ source in connection with decarbonated platform sediments (Lee and others, 2013; Lee and Lackey, 2015). For example, during the dispersal of Pangea, the initiation of continental arcs in the Neo-Tethys regime overlapped the culmination of circum-Pacific arcs in Cretaceous-Paleocene (Cao and others, 2017).

We use the global surface area addition rate of granitoids (2-D; Cao and others, 2017) to approximate the magma emplacement rate at continental arcs (3-D), which is a better proxy than the 1-D arc lengths. For a conservative estimate, we do not apply
preservation correction, so older arcs are relatively under-represented due to erosion (Cao and others, 2017). Based on the present carbon input, the evolution of surface area rates, and the linear relationship between CO₂ release and magma emplacement, we extrapolate the CO₂ input from carbonate contact metamorphism to the whole Phanerozoic (fig. 9B). The CO₂ outgassing from mid-ocean ridges, which scales with the mid-ocean spreading rate (Berner, 1991), is also plotted for comparison (fig. 9B). We note that our model prediction is a lower-limit estimate of CO₂ input from continental arcs, but the contribution is comparable to mid-ocean ridges in Early Triassic that followed the Permian icehouse interval, and during the late Mesozoic greenhouse interval (fig. 9).

In the long-term carbon-cycle model GEOCARB (Berner, 1991, 1994; Berner and Kothavala, 2001), the tectonic outgassing of CO₂ scales with the seafloor spreading rate that represents global tectonic activities. Qualitatively, the rates mid-ocean ridge spreading and plate convergence are positively correlated; greater tectonic activity accelerates CO₂ release by volcanism and metamorphism (Berner and others, 1983; Lasaga and others, 1985). The CO₂ input from continental arcs is a function of arc magmatic emplacement rate, which also depends on the plate configuration (Lee and others, 2013; McKenzie and others, 2016; Cao and others, 2017). During cycles of supercontinent dispersal and amalgamation, the continental arcs internal to the supercontinent increases or decreases the length of arcs, respectively (Cao and others,
2017). For example, the Cretaceous-Paleocene greenhouse interval was concluded by the Paleogene closure of the Tethys Ocean which substantially reduced the global continental arc length (fig. 7C; Lee and others, 2013; Van Der Meer and others, 2014). Once arc magmatism ceases, the continuous orogenic uplift exposes fresh and highly weatherable continental materials so that the fossil arcs could act as a chemical weathering sink (Lee and others, 2015; Jiang and Lee, 2018). Field-based studies are needed to evaluate both effects that are to be incorporated into revised long-term carbon cycle models in the future.

CONCLUSIONS

We present a numerical simulation of infiltration-driven contact metamorphism in a simplified model CaO-SiO$_2$-H$_2$O-CO$_2$ system, taking into account the reaction kinetics, silicate dissolution, and porosity evolution. The modeling results and analytical analysis show that the reaction front lags the fluid infiltration front and propagates at the rate \[ \frac{[\text{infiltrating fluid flux}]}{H11003} \times \left(\frac{[\text{fluid carbon content in equilibrium}]}{[\text{rate-limiting reactant}]}\right) . \] The steady-state carbon flux yields a linear relationship with the infiltrating flux, and is largely independent of other factors.

The global CO$_2$ outgassing from continental arcs can be approximated using a linear relationship with the emplacement rate of granitoid magma. The estimate of present-day CO$_2$ release from continental arcs is about 0.06–0.9 Tmol yr$^{-1}$, about half-to-one orders of magnitude smaller than the volcanic CO$_2$ of arcs (1.3–3.1 Tmol yr$^{-1}$; Sano and Williams, 1996; Marty and Tolstikhin, 1998; Hilton and others, 2002).

Although the estimate of CO$_2$ input from continental arcs is conservative, the CO$_2$ release via fluid-infiltration-induced metamorphic decarbonation by Cretaceous-Paleocene arc flare-ups could alone be comparable to the mid-ocean ridge outgassing. Thus, this study supports the hypothesis that enhanced continental arc activities drive warming over geologic timescales, especially during the late Mesozoic-early Cenozoic greenhouse interval (Lee and others, 2013; Lee and Lackey, 2015). Similarly, when magma intrudes organic-rich sediments, a large volume of greenhouse gas CH$_4$ could be released over a short timescale (Aarnes and other, 2010).

In nature, both carbonate dissolution, metamorphic decarbonation and magmatic assimilation operate in parallel to shape distinctive petrologic features that vary from one outcrop to another. Further efforts will be required incorporating models of electrolyte fluid (Sverjensky and others, 2014; Miron and others, 2017) to couple dissolution and decarbonation to evaluate the extent of CO$_2$ in the metasomatic fluid. The field-based studies, in association with sophisticated simulations specific to observed assemblages, will be essential for a better time-resolution of metamorphic decarbonation at continental arcs.

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