

Global Continental Arc Flare-ups and Their Relation to Long-Term Greenhouse Conditions

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Continents are long-term storage sites for sedimentary carbonates. Global flare-ups in continental arc volcanism, when arc magmas intersect and interact with stored carbonates, thus have the potential for elevating the global baseline of deep Earth carbon inputs into the atmosphere, leading to long-lived greenhouse conditions. Decarbonation residues, known as skarns, are ubiquitously associated with the eroded remnants of ancient batholiths, attesting to the potential link between continental arc magmatism and enhanced global CO₂ inputs to the atmosphere.

KEYWORDS: arc magmatism, carbonates, climate change, greenhouse gas, CO₂

INTRODUCTION

The dominant control on Earth's long-term (>1 My) climate variability is the amount of greenhouse gases, primarily CO₂, in the atmosphere (Walker et al. 1981). On these long timescales, the amount of carbon in the Earth's atmosphere, hydrosphere, and biosphere (termed the "exogenic system") is controlled by CO₂ fluxes to and from the crust and mantle (the "endogenic system"; Berner 1991). Additions of CO₂ to the exogenic system come from volcanism, metamorphism, and weathering of fossil organic carbon and carbonates (Berner 1991; Petsch 2014). Volcanic inputs of CO₂ include those from mid-ocean ridges, intraplate magmatism ("hotspots"), and volcanic arcs above subduction zones. Metamorphic CO₂ additions come from degassing processes associated with continental collisional orogenies and magmatically active continental margins. Outputs of CO₂ from the exogenic system are from silicate weathering and biological activity in the form of carbonate and organic carbon burial. All of these outputs scale with the amount of CO₂ in the atmosphere, and, thus, serve as negative feedbacks that regulate the amount of carbon in the exogenic system (Walker et al. 1981). Because the amount of carbon in the Earth's interior is orders of magnitude larger (10³–10⁴ times) than that in the exogenic system (Dasgupta and Hirschmann 2010), net inputs from the Earth's interior to the exogenic system over long timescales are generally independent of the exogenic system. Thus, to a first approximation, volcanism and metamorphism are commonly taken as external forcings of the exogenic carbon cycle on long (>1 My) timescales (Berner 1991). In contrast, volcanic and metamorphic fluxes play insignificant roles in modulating climate on short (<10–100 ky) timescales because carbon exchange fluxes between reservoirs within the exogenic system (e.g. hydro-

sphere, atmosphere, biosphere) are 10³–10⁴ times higher than the fluxes of carbon between the deep Earth and the exogenic system. To put some of these CO₂ fluxes in context, anthropogenic emissions from burning of fossil fuels and cement production are 10⁴–10⁵ times greater than the volcanic fluxes.

In this article, the focus is on long-term (>1 My) climate variability, so the discussion is confined only to deep-Earth inputs of carbon

into the exogenic system. Of critical importance is why these deep-Earth forcings vary with time. Most attention has been focused on variations in the rates of oceanic crust and large igneous province production (Berner 1991; Larson 1991). For example, greenhouse conditions during the Cretaceous are traditionally thought to have been driven by enhanced rates of plate spreading and a higher frequency of flood basalts (Larson 1991). Less attention has been given to the possibility that magmatic arc (subduction zone) volcanoes influence long-term climate variability. However, the amount of CO₂ exiting magmatic arcs, particularly continental arcs, is probably large. Here, we show that variations in the length and distribution of continental arcs may play an important role in modulating long-term climate.

SOURCES OF CO₂ IN ARC MAGMAS

Estimated fluxes of CO₂ (in terms of teragrams per year of carbon, Tg/y) are 18–37 Tg/y for modern magmatic arcs (Dasgupta and Hirschmann 2010), 12–60 Tg/y for mid-ocean ridges (Hilton et al. 2002), 1–30 Tg/y for oceanic intraplate volcanoes (Marty and Tolstikhin 1998) (Fig. 1A). Carbon exchange rates *within* the exogenic system (i.e. between the biosphere, atmosphere, and ocean) are two orders of magnitude larger than the above magmatic fluxes, which means that the residence times of carbon in the exogenic reservoirs are on the order of days to 1000 y, and, therefore, that these internal exchanges are not important for carbon cycling at >1 My timescales (Fig. 1). Volcanic CO₂ flux estimates nevertheless remain uncertain, particularly for magmatic arcs, because the outgassing of CO₂ through arc volcanoes is spatially heterogeneous and episodic on short (<1 My) timescales, making it difficult to obtain meaningful averages from localized studies. However, the CO₂ flux through magmatic arcs is probably several times greater (~150 Tg/y of C) than that cited above if the diffusive flux through volcanic edifices is accounted for (Burton et al. 2013). By comparison, the flux of CO₂ from oxidative weathering of organic carbon is ~60 Tg/y of C (Petsch 2014).

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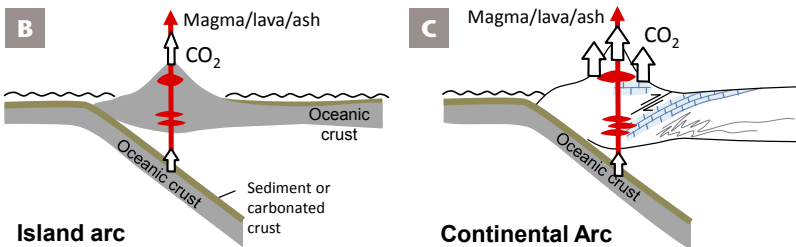
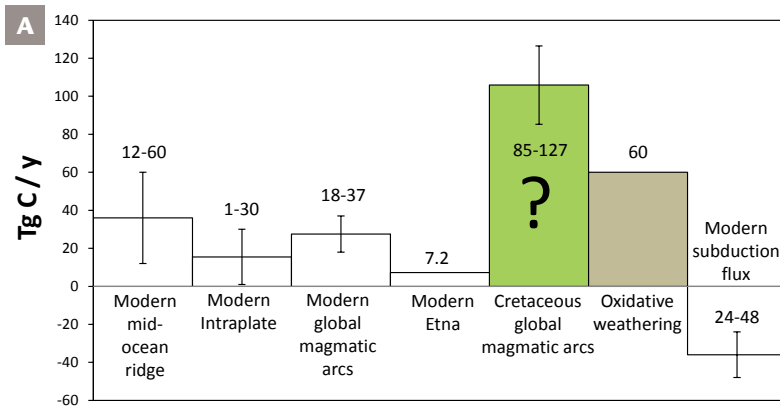


FIGURE 1 CO₂ sources and fluxes. **(A)** Inputs of CO₂ (in teragrams carbon per year, i.e. 10¹² g/y) into the exogenic system from the endogenic system (crust and mantle). Modern volcanic inputs are shown for global mid-ocean ridge, intraplate, and subduction zone volcanoes, the latter of which we refer to as magmatic arcs and include both island (intraoceanic) and continental arcs (Marty and Tolstikhin 1998; Hilton et al. 2002; Dasgupta and Hirschmann 2010; Burton et al. 2013). The CO₂ inputs from Mount Etna (Italy) are from the intersection of its volcanic products with crustal carbonates (Allard et al. 1991). Estimated subduction flux of carbon at the trench is shown as a negative quantity (Dasgupta and Hirschmann 2010). For comparison is an estimate of the total CO₂ flux out of the global Cretaceous arc system where the continental arc length was longer than in the mid-Cenozoic, based on estimates of Lee et al. (2013), assuming 25% more carbonate-intersecting continental magmatic arcs and ~10% effective assimilation of or reaction with pure carbonate. Estimate of CO₂ release via oxidative weathering of fossil organic carbon is also shown (Petsch 2014). Error bars represent maximum and minimum bounds on various estimates of CO₂ inputs if available. **(B, C)** Cartoons showing the different sources of carbon in subduction zones. Continental arcs have more carbonates within the upper plate due to storage of ancient carbonates on continental margins over Earth's history. White arrows represent fluxes of CO₂ and red arrows represent magmas.

There are three sources of CO₂ in arc magmas: subducted carbon in sediments and carbonated oceanic lithosphere, background carbon in the mantle wedge, and carbon and carbonated oceanic lithosphere, from background carbon in the mantle wedge, and from carbon in the overlying arc crust (upper plate). Estimates of the modern global subduction flux of carbon ranges from 24 to 48 Tg/y (Dasgupta and Hirschmann 2010), which is, within error, indistinguishable from the arc flux cited above, and possibly lower if one accounts for the diffusive CO₂ flux through arcs. There is, however, debate over how much of the subducted carbonate decarbonates during subduction. One view is that much of the carbonate in subducting slabs remains stable beyond the depths of arc magma generation because slabs, at least today, appear to be too cold for efficient decarbonation (Kerrick and Connolly 2001; Dasgupta and Hirschmann 2010) (FIG. 2A). Decarbonation, however, can be amplified if the slab is fluxed with water, presumably derived from dehydration reactions in the deeper parts of the slab (Ague and Nicolescu 2014). Addition of water would decrease CO₂ activity (X_{CO_2}) and the temperature required for decarbonation (FIG. 2A). A further possibility is that a significant component of the arc CO₂ flux is derived from the upper plate via interactions of carbonated crust or sediments with magmas. Such a scenario was recently demonstrated for Merapi volcano in the Indonesian arc (Troll et al. 2012). Not only are the temperatures required for decarbonation in the upper plate lower (lower pressure), but magmas also provide the much-needed heat to drive such reactions.

But how do CO₂ fluxing through arcs and the sources of such CO₂ change through time on a global scale? One possibility is to vary global plate convergence rates, but exactly how this would translate into volcanic CO₂ outgassing is unclear. Rapid convergence rates might favor more mantle-wedge upwelling, increasing the magmatic flux associated with decompression melting and thereby increasing the mantle contribution of CO₂. However, the thermal gradient followed by a rapidly descending slab would be depressed, decreasing the efficiency of decarbonation (FIG. 2A). Similarly, slow convergence rates would increase the efficiency of slab decarbonation but would decrease the mantle contribution because of decreased

mantle-upwelling rates. A second mechanism is to change the average age, and hence thermal state, of a subducting slab, which might influence the efficiency of slab decarbonation. A third possibility is that the carbon content of subducting sediments and oceanic lithosphere changes with time (Johnston et al. 2011). Yet another possibility is that the nature of the upper plate, and by implication the amount of crustal carbon intersected by arc magmas, changes with time (Lee et al. 2013).

FLARE-UPS AND OSCILLATIONS BETWEEN CONTINENTAL- AND ISLAND ARC-DOMINATED STATES

There is considerable evidence that magmatic production in arcs is not constant in either space or time (Paterson and Ducea 2015 this issue). Long segments of continental arcs can simultaneously flare up within a ~50 My window, accompanied by arc-front migration away from the trench that culminates in a magmatic hiatus (Haschke et al. 2002). In some cases, this magmatic hiatus is followed by a rapid renewal of arc magmatism back towards the trench, initiating another cycle of flare-ups and arc-front migration (Ducea and Barton 2007; DeCelles et al. 2009). There is also a growing appreciation that the global length of continental arcs varies with time (Lee et al. 2013). For example, between ~150 and 55 Ma, continental arcs extended from South America through North America and into eastern Siberia and the southern and eastern margins of Eurasia (FIG. 3). In the eastern Pacific, continental arc magmatism along the North American Cordillera declined substantially after ~70 Ma (Lipman 1992). Those continental arcs along the southern margin of Eurasia terminated at ~50 Ma with the closure of the Tethys Ocean and the inception at ~52 Ma of the Tonga, Kermadec, Marianas, Izu-Bonin island arc system in the western Pacific (Ishizuka et al. 2014). Altogether, the length of continental arcs in the Cretaceous and early Paleogene may have been twice the length of continental arcs developed since the mid-Cenozoic (Lee et al. 2013). Global increases in continental arc magmatism may also have taken place during the Cambrian, based on detailed analysis of detrital zircon data (McKenzie et al. 2014). Oscillations between continental- and island

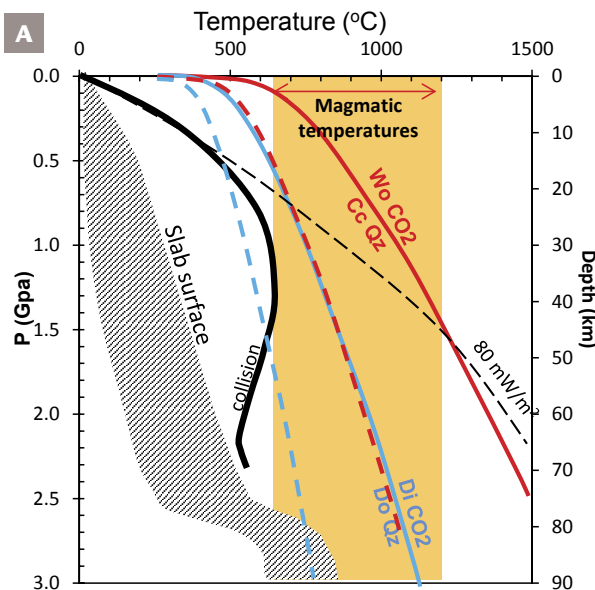


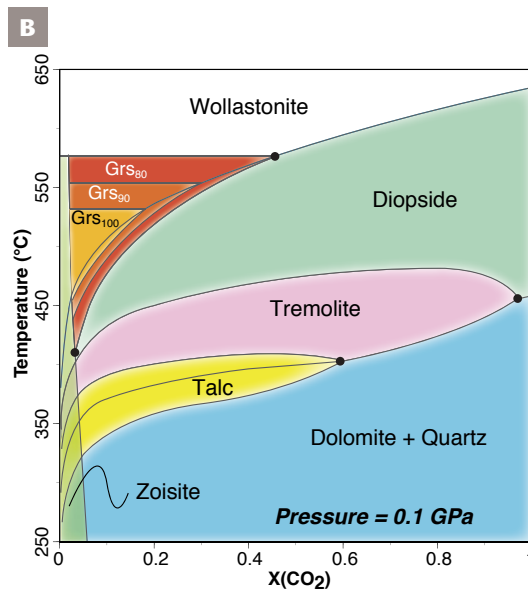
FIGURE 2 (A) Temperature of decarbonation reactions (1) (red lines) and (2) (blue lines) described in the text at $X_{\text{CO}_2} = 1$ (solid) and $X_{\text{CO}_2} = 0.1$ (dashed) as a function of pressure (MODIFIED FROM LEE ET AL. 2013). Also given are magmatic temperatures shown by orange field, slab surface temperatures ranging from hot and cold slabs shown by the hatched area, a geotherm associated with continent–continent collision shown as a black line, and an equilibrium conductive geotherm for a surface heat flow of 80 mW/m^2 shown as a black dashed line. Decarbonation in subducting slabs can only occur if the system is fluxed by large

arc-dominated states could potentially have profound impacts on long-term carbon cycling and, hence, climate variability.

Why would the nature and activity of subduction zone volcanism change with time? Increase in plate convergence is an obvious mechanism for driving flare-ups, but only weak correlations have so far been reported (Ducea 2001). Repeated shallowing and steepening of slabs may also be important (Haschke et al. 2002), though no general and globally synchronous mechanism for such a process has been successfully proposed. Another possibility invokes surges in compression of the upper continental plate in response to rapid lower-crustal delamination events, causing underthrusting of back-arc continental rocks and subsequent crustal melting (DeCelles et al. 2009). Magmatic arc flare-ups, particularly in continental arcs, may also be due to decompression melting within the mantle wedge, the extent of which is modulated by the thickness of the upper plate, which in turn is controlled by cycles of magmatic thickening and dynamic thinning (Karlstrom et al. 2014). As for what drives the Earth to oscillate between continental- and island arc-dominated states, it has been speculated that dispersal of continents may induce the leading edges of continents into compression, resulting in a transition from island arc to continental arc (Lenardic et al. 2011; Lee et al. 2013). Likewise, during the aggregation of continents, ocean–continent convergent margins are placed into extension, culminating in the transition to an intraoceanic arc.

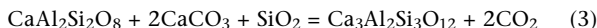
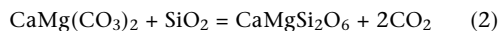
EVIDENCE FOR INTERACTION OF CRUSTAL CARBONATES WITH ARC MAGMAS

Whatever the cause of these changes in subduction zone dynamics, magmatic arc flare-ups and prolonged intervals of increased continental arc length should have profound impacts on the global magmatic flux of CO_2 . The amount of carbonate stored in continents is at least 10 times greater (and more concentrated) than that stored in oceanic crust



amounts of water, such that X_{CO_2} is less than 0.1 (Ague and Nicolescu 2014), because the slab is cold. In contrast, note the importance of hot magmas in driving decarbonation reactions. (B) Simplified T - X_{CO_2} diagram illustrating stability fields of certain minerals in the CaO - MgO - SiO_2 - Al_2O_3 - CO_2 system with excess calcite and quartz. Note that as X_{CO_2} decreases (presumably due to an increase in water activity), decarbonation reactions occur at lower temperature. Decreased CO_2 activity also stabilizes garnet and wollastonite relative to diopside. The garnet field is expanded as the Fe content in calcic garnet increases.

(Hayes and Waldbauer 2006): most carbonates accumulate on shallow continental margins, which tend not to subduct (FIG. 3). Oscillations between continental and island arc states (FIG. 1B AND C), thus, have the potential to drive profound variations in CO_2 fluxing through arcs if there is sufficient interaction between arc magmas and the overriding crust (Lee et al. 2013). Magmas interacting with carbonates are known to produce reactions that release CO_2 and form calc-silicate residues (skarns). For example, wollastonite, diopside, and garnet skarns represent the end-products of the following decarbonation reactions (FIG. 2),



The SiO_2 involved in the reactions is either intrinsic to the metasedimentary wallrock or introduced via magmas and hydrothermal fluids. If infiltration of magmatic silica causes complete decarbonation of a pure dolostone or limestone by reactions (1) and (2), approximately 1350 and 1190 kg, respectively, of CO_2 are released for every cubic meter of carbonate—a huge yield of CO_2 (equaling 90% of the weight of a common hybrid automobile).

Excellent examples of direct and indirect magma–crustal carbonate interactions can be found in the Sierra Nevada and Peninsular Ranges batholiths in western North America, which represent one segment of a Jurassic to Paleogene circum-Pacific system of continental arcs (FIG. 3). These batholiths were constructed mostly of Cretaceous plutons emplaced through late Paleozoic through early Mesozoic island arc terranes in the west and through Proterozoic to Paleozoic cratonic basement and associated platform sediments in the east (Ducea and Barton 2007). Carbonate-bearing metasediments, ranging from nearly pure marbles to carbonate-bearing siliciclastic protoliths are laterally and vertically extensive, occurring from subvolcanic to uppermost mantle paleodepths. These carbonated wallrocks have

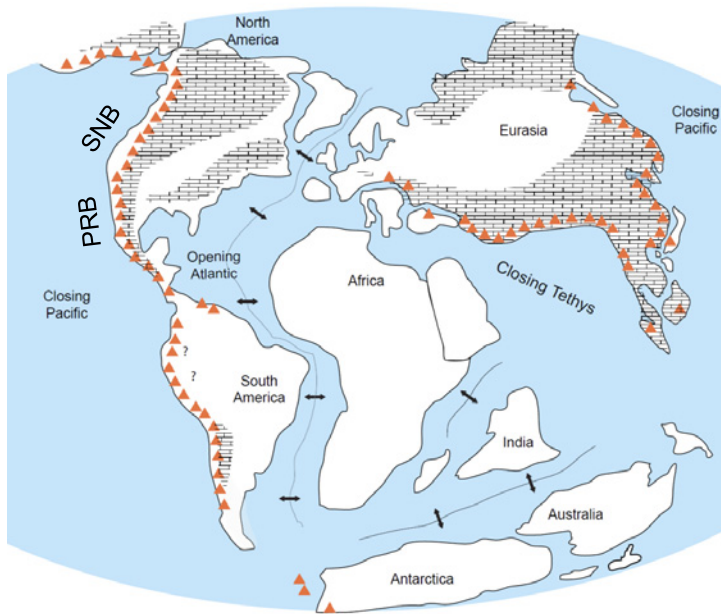


FIGURE 3 Cretaceous paleogeography showing locations of continental arcs and pre-Cretaceous carbonate platforms through which magmas may have intersected (this is a minimum bound on carbonate distribution in continents because Precambrian carbonates are not shown). SNB—Sierra Nevada Batholith; PRB—Peninsular Ranges Batholith. FIGURE MODIFIED FROM LEE ET AL. (2013)

been variably decarbonated by the plutons, via thermal and metasomatic effects, producing skarns. Qualitatively, based on mapping the skarn indicator mineral scheelite (CaWO_4 ; Lee et al. 2013), Cretaceous skarn formation in the North American Cordillera was extensive (FIG. 4).

Extreme decarbonation is observed in cases where fluxing of hydrous fluids associated with shallow hydrothermal systems has occurred (D’Errico et al. 2012). For example, calc-silicate and carbonate-bearing pelitic and quartzofeldspathic metasediments distributed between plutons as screens and roof pendants are abundant and show evidence for pronounced decarbonation reactions (FIG. 5). Indirect magma-carbonate interaction also occurs during regional metamorphism of the lower crust (at or below 45 km), which appears to be coeval with magmatism (FIG. 6) as evidenced by marble and calc-silicate lenses interleaved with metaquartzitic restites and migmatites in the southern Sierra Nevada and eastern Peninsular Ranges (FIG. 6F). Exactly how supracrustal rocks, including carbonates, are transported to lower crustal levels is unclear, but recent thermobarometric and geochronologic work suggests that North American basement and overlying sediments were thrust deep beneath the arc during peak magmatism, perhaps along a retro-arc thrust (Chin et al. 2013). Although the CO_2 -per-gram that is produced from regionally metamorphosed metasediments is low, the affected volume of rock is greater, perhaps by 100 times, than for skarn.

Finally, direct carbonate-magma interaction can be found in the plutons themselves. Endoskarns (carbonate reaction products within the margins of the pluton) and abundant mafic xenoliths of calc-silicate origin attest to assimilation and reaction with carbonate-bearing wallrocks (FIG. 6).

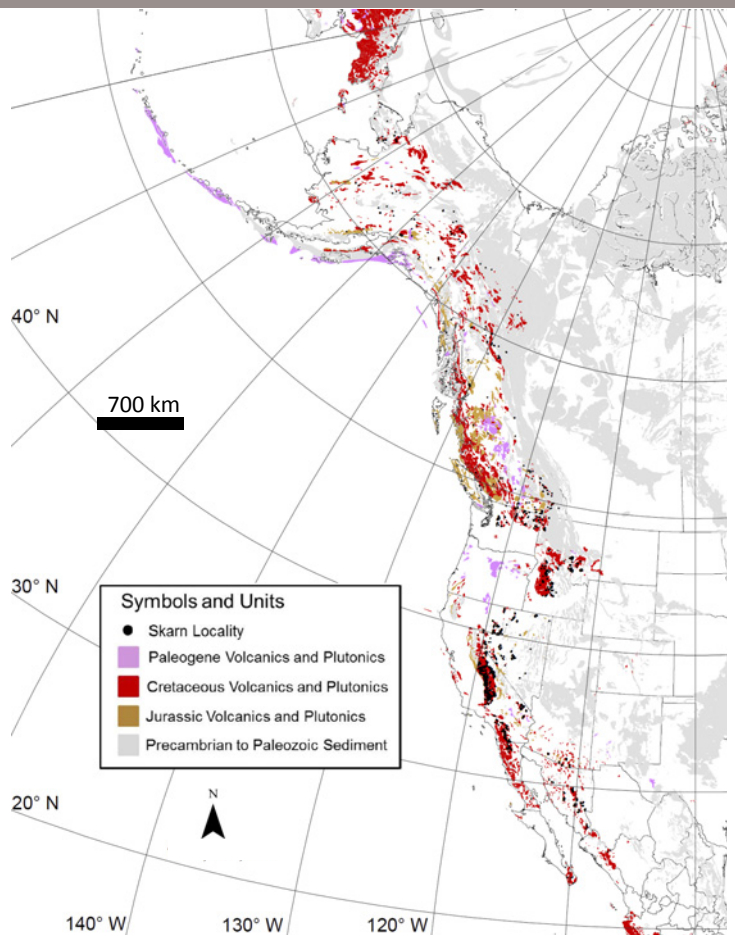


FIGURE 4 Map of the North American Cordillera showing distribution of Jurassic, Cretaceous, and Paleogene magmatic rocks along with occurrences of Ca-tungstate (CaWO_4 , scheelite), a base metal ore found in many skarns. MAP ADAPTED FROM LEE ET AL. (2013)

EFFICIENCY OF DECARBONATION IN THE UPPER PLATE

The efficiency of upper-plate decarbonation depends on several factors. High temperatures are clearly important, but there are two confounding factors. First, the temperature of decarbonation increases with increasing pressure, meaning that more heat is required to drive decarbonation reactions in subducting slabs than in the upper plate (FIG. 2A). Second, Le Chatelier’s principle, when applied to any decarbonation reaction, shows that the lower the CO_2 activity, the greater the extent of metamorphic reaction. In other words, any CO_2 -producing reaction acts to stifle further reaction progress unless metamorphic temperature increases or unless another fluid (typically H_2O) is introduced to dilute and remove CO_2 from the site of reaction (FIG. 2B). Evidence of wollastonite formation by reaction (2) is well illustrated in the Mount Morrison roof pendant in which vertical infiltration of water-rich fluids created sharp boundaries between protolith domains and wollastonite-bearing rocks (FIGS. 5A–G). Extreme decarbonation can also produce massive garnetite (reaction 3; FIG. 6E–F) by extensive fluxing of hydrous fluids associated with shallow hydrothermal systems (D’Errico et al. 2012). In part, this occurs because H_2O almost always exsolves from a silicate melt when the melt cools and crystallizes. But more importantly, high permeability in the upper crust permits the hydrothermal circulation of magmatic fluids and/or meteoric waters. All of these conditions are enhanced in the upper plate of magmatically active subduction zones but are suppressed in subducting slabs (cold and high pressure), in the forearc (cold), and in magma-poor continent-continent collision zones (dry and cold).

IMPLICATIONS FOR CLIMATE AND FUTURE DIRECTIONS

Ultimately, high CO₂ fluxes in magmatic arcs should be linked to the availability and reactivity of crustal carbonates. These carbonates can be either tapped by plutons that ascend to shallow levels in the arc crust (presumably during the early stages of the arc), or tapped during later arc stages when carbonates are transported into the lower crust of a thermally matured arc. If this latter carbonate transport is via contractional deformation within arcs, then there should be a relationship between crustal carbonate quantity, arc magmatic flare-ups, and CO₂ production, all of which are possibly tuned by overarching tectonic controls and the growth of the crustal carbonate reservoir over the history of the Earth. The implications for long-term climate variability are potentially profound. Mount Etna (Italy) is one of the few currently active volcanoes whose volcanic products intersect carbonates. It alone can account for 20% of the total modern arc addition of CO₂ to the exogenic

system (FIG. 1A). The presence of a circum-Pacific length of continental magmatic arc during the Cretaceous could have profoundly increased CO₂ inputs, possibly explaining or, at the very least, contributing significantly to, the greenhouse conditions that were prevalent at that time (FIG. 2). Lee et al. (2013) estimated that the total flux of CO₂ from the extended length of Cretaceous–Paleogene continental arcs could have been ~3–5 times that of the present global arc CO₂ flux (FIG. 1A).

Many questions, however, remain unanswered. What conditions favor continental and island arcs? What drives flare-ups in arc magmatism? How do flare-ups modify the thermal state and thickness of the upper plate? Has the size of the continental carbonate reservoir changed with time? How are carbonates emplaced into the deep crust? Can we use field observations, thermal modeling (Barton and Hanson 1989), and modeling of hydrothermal systems to better quantify the extent to which crustal carbonates decarbonate? How much does the upper plate contribute

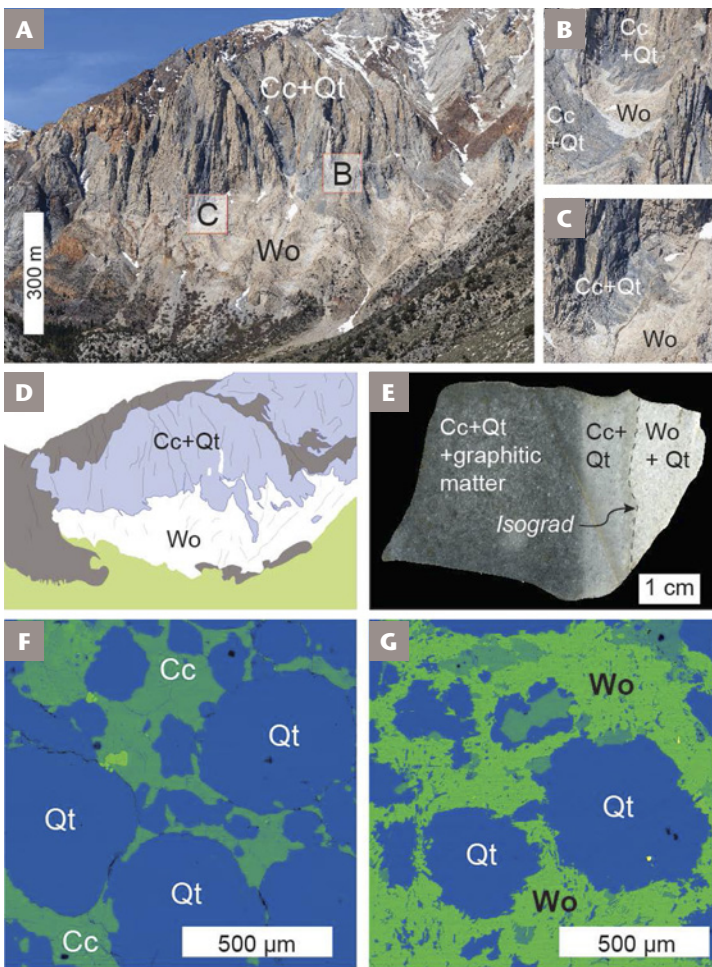


FIGURE 5 Production of wollastonite (Wo) by decarbonation reaction (1) in the calcite (Cc)-cemented Mount Morrison quartz (Qt) arenite sandstone, east central Sierra Nevada, California (USA). Viewed at scales ranging from 0.001 cm to 1 km. (A–E) Reaction (1) is virtually complete, exhausting almost all calcite, in parts of the vertically oriented fluid-flow system, with the sharp boundary between Wo-bearing and Cc + Qt rocks showing the importance of water in diluting CO₂ and promoting metamorphic reaction. In addition, carbon contained in graphitic matter is released as either CO or CO₂ as it is oxidized by infiltrating water. (F–G) False-colored backscattered-electron images show typical pre- and postreaction sandstones with ~25 vol% Cc in the original rocks being decarbonated during wollastonite crystallization. Images for panels A–C from a Gigapan® image. COURTESY: DR. RONALD SCHOTT

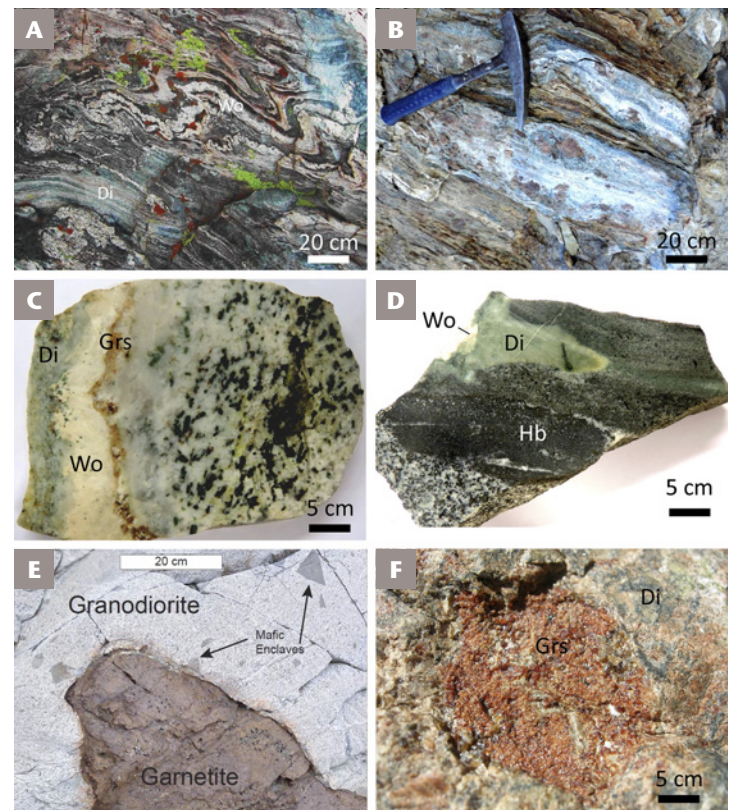


FIGURE 6 Examples of carbonate residues from the Peninsular Ranges and Sierra Nevada Batholith in California (CA). (A) Strongly folded carbonated metasediments on the margin of a tonalite pluton in Riverside, CA (USA). Dark gray to green bands are diopside-rich and white bands are wollastonite- or calcite-bearing (light green and orange splotches are lichen). (B) Grossular-diopside band within migmatized metasediments, representing an example of decarbonation during regional metamorphism (eastern San Jacinto Mountains, CA, USA). (C) Reaction zone across the contact between a metacarbonate xenolith (left) entrained within a tonalite pluton (right) from the Domenigoni Valley pluton, Menifee, CA (USA). Gradation from diopside (Di) to grossular (Grs) to wollastonite (Wo) reflects decreasing CO₂ activity and increasing Al₂O₃ activity towards the tonalite. The outer margin of the tonalite has been modified into an endoskarn as evidenced by the conversion of hornblende to diopside while retaining magmatic textures. (D) Another example of a calc-silicate metasedimentary xenolith within the same tonalite body in C. The core of the xenolith is represented by wollastonite and diopside, but outer margins have been transformed into hornblende (Hb) due to an increase in H₂O activity. (E) Massive garnetite adjacent to granodiorite in Mineral King pendant, Sierra Nevada, CA (USA). (F) Typical grossular-andradite rich garnetite (with minor diopside) from near the location of F.

to CO₂ compared to the subducting slab or the background mantle wedge in arcs? How much CO₂ escapes to the atmosphere or reprecipitates as secondary carbonate in the crust? What isotopic or elemental tracers could constrain temporal changes in continental versus island arc activity and/or the formation of skarns?

In summary, we speculate that global continental arc flare-ups may play a role in driving long-term greenhouse conditions. However, the nature of the negative feedback (i.e. the overall kinetics of chemical weathering) must also be considered. Continental magmatic arcs define some of the highest elevations on Earth; therefore, orographically induced precipitation could increase the efficiency of weathering and thereby counter the increase in volcanic CO₂ addition to the exogenic system. There is an overlap between the records of arc-related sedimentary detrital zircons and plutonic magmatic zircons, which suggests that arc magmatism, uplift, and erosion/weathering are coupled (Paterson et al. 2011; Paterson and Ducea 2015). However, it is not known whether magmatism, uplift, and weathering are actually in phase or whether there is significant and continuing chemical weathering of newly formed continental arc crust well after the end of magmatism and CO₂ fluxing. High elevations and high exhumation rates are thought to have persisted long after Sierra Nevada arc magmatism terminated (Poage and Chamberlain 2002).

If this delay in weathering is a general phenomenon of continental arcs, the question arises as to whether global flare-ups in continental arcs are not just drivers of greenhouse climates but also facilitators of subsequent icehouse climates. An icehouse climate could result from the generation of large areas of juvenile crust that would be amenable to chemical weathering and drawdown of CO₂. And long hiatuses in continental arc magmatism during the Neoproterozoic could also be associated with icehouse, or even snowball, conditions (McKenzie et al. 2014). Thus, we see a bright future for studies that integrate outcrop-to-regional field studies of magmatic arcs with geodynamics, volcanology, geomorphology, and climate.

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