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Decarbonation efficiency in subduction zones: Implications for warm Cretaceous climates

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ABSTRACT

Subduction zones play a fundamental role in the geochemical cycle of carbon, and related arc volcanism is believed to exert primary control on atmospheric CO_2 concentrations over geological time. Arc volcanism may have been particularly important in the most recent Greenhouse of the late Cretaceous, where it has been hypothesized that the subduction of the carbonate-rich Tethys contributed to overall higher volcanic CO_2 outgassing rates and thus a warmer climate. To test this hypothesis, the decarbonation efficiencies of modern subduction zones were calculated through a geochemical database that compared subaerial arc CO_2 fluxes with the subducting crust and sediment geochemistry. The modern data are used to postulate a CO_2 recycling and degassing scenario for arc volcanism related to the closure of the Tethys. Our analysis indicates that the thermal structure of subduction zones controls the extent and depth of slab decarbonation, while the sediment geochemistry (e.g. the amount of carbonate sediment) may be of secondary importance. The calculated decarbonation efficiency of modern arcs ranges from 18 to 70%. Our calculations support recent models predicting carbon recycling through infiltration-driven decarbonation, and limited by water availability at sub-arc depths. This analysis allows us to make inferences about the potential volcanic CO_2 flux from subduction of the Tethys during the Cretaceous, suggesting between an 8 and 222% increase over modern CO_2 outgassing. We suggest that the primary reason for the increase in CO_2 outgassing in the Cretaceous is contamination of arc magmas by platform carbonates in the overlying crust and increased decarbonation efficiency.

1. Introduction

On geological timescales the concentration of carbon dioxide (CO_2) in the atmosphere is regulated by a dynamic equilibrium between outgassing from volcanoes, consumption by chemical weathering of silicate minerals, and deposition of calcium carbonate in the ocean (Berner and Lasaga, 1989; Berner et al., 1983; Walker, 1986). The consumption of atmospheric CO_2 through the chemical weathering of silicate minerals leads to the precipitation of carbonate minerals in the ocean, removing carbon from the ocean–atmosphere system through the following generalized reaction:

$$CaSiO_3 + CO_2 + 2H_2O \rightarrow CaCO_3 + H_4SiO_4$$

The destruction of oceanic lithosphere at subduction zones partially recycles the carbon it contains (in both the crust and overlying sediment) back into the atmosphere, while a remaining proportion is retained in the slab and transferred to the deep mantle or remain in the accretionary wedge (Berner et al., 1983). Subduction zones thus play a fundamental role in the geochemical cycle of carbon, as well as other major volatiles, and may have exerted control over atmospheric CO_2 concentrations over geological time scales (Edmond and Huh, 2003; Rea and Ruff, 1996).

Geochemical thermometers, such as oxygen isotopes in carbonate minerals and fossils, have long suggested that the late Cretaceous and early Cenozoic (~120 to 34 Myr) were much warmer than our modern climate (Norris and Wilson, 1998; Zachos et al., 2001). Furthermore, paleo-pCO_2 proxies (Cerling, 1991; Pagani, 2002; Pagani et al., 2005a), modelling (Pollard and DeConto, 2005), and paleo-pH proxies (Pagani et al., 2005b; Pearson and Palmer, 2000) suggest that it was elevated atmospheric CO_2 concentrations in the late Cretaceous to early Cenozoic that contributed to this substantially warmer world. The cause of the elevated pCO_2 remains somewhat enigmatic, but recent work has suggested that the subduction of the Tethys ocean during the northward equatorial convergence of India with Eurasia may have been the strongest contributing factor (Edmond and Huh, 2003; Kent and Muttoni, 2008). Enhanced pelagic carbonate accumulation in the Tethys (van Andel, 1975), coupled with a fast convergence rate of the Tethys with Eurasia, may have resulted in prolonged release of excess CO_2 in the subduction-associated arc volcanoes. This, coupled with lower silicate weathering rates due to lack of topographic highs such as Himalayan and Cordilleran belts (Edmond and Huh, 2003), could hypothetically be the primary mechanism for this sustained high pCO_2.

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It is unclear, however, that previous attempts at quantifying Cretaceous arc CO_2 emissions have properly accounted for important sub-arc processes such as the effect of a changing geotherm with crustal age and the potential impact of crustal contamination on the net CO_2 output. While by first principles, the more carbon you put down the more you will get out, the ultimate controls on total carbon degassing in subduction arc volcanoes are more nuanced and deserve a more rigorous analysis. This study aims to quantify the potential CO_2 output from the Tethyan subduction zone based on a detailed analysis of the modern geochemical and physical relationship between subduction and related volcanic CO_2 emissions. We first address the primary factors that govern decarbonation (release of carbon from slab to mantle wedge) at subduction zones. Using arc volatile flux data from recent studies (Fischer, 2008; Hilton et al., 2002) along with the input slab geochemistry (Plank and Langmuir, 1998) this study will estimate independently the decarbonation efficiency of arcs worldwide. After examining the physical parameters that control the decarbonation efficiency of modern arcs, we apply our results to ancient arcs to quantify the potential volcanic CO_2 output related to the Tethyan subduction zone. The predicted physical parameters constraining Tethyan subduction are used to estimate a range of possible decarbonation efficiencies that, once combined with the estimated carbon content of the subducting slab, produce a range of potential CO_2 emissions from the Tethys and the late Cretaceous/early Cenozoic global subduction systems.

2. Background

Typical oceanic lithosphere is comprised of three distinct layers, each containing H_2O and CO_2 chemically bound in hydroxylated and carbonated minerals respectively, that were acquired during the time that the lithosphere spent in contact with the hydrosphere. Upon subduction, this H_2O and CO_2 can be released (in the forearc — shallow depth during subduction — or at subarc depths) or subducted into the mantle. The amount that is released versus subducted depends largely on the thermal structure of the lithosphere during subduction, which relates to both the dynamics in the subduction zone and the age of the ocean crust when it is subducted (Dasgupta and Hirschmann, 2010). We will first review the amount of volatiles in the various layers of oceanic lithosphere and how they were acquired, then discuss the mechanism and controls on devolitilization during subduction.

The base of the oceanic lithosphere is comprised of harzburgite/peridotite lithospheric mantle and remains largely unhydrated during most of its transit at the surface of the Earth. Bending of the plate during subduction, however, creates large normal faults that allow water to infiltrate this layer to 15–50 km depth and form serpentine (13 wt.% H_2O (Peacock, 2001; Rupke et al., 2004)). The more brittle this lowest layer of ocean lithosphere, the deeper normal faults can penetrate, and thus higher water content it will ultimately contain when it is subducted (Rupke et al., 2004). Overlying this lithospheric mantle is the "oceanic crust," which is the result of partial melting at mid ocean ridges that creates a 7 ± 1 km thick section of mafic rocks. Hydrothermal alteration of the oceanic crust at mid ocean ridges produces various hydrous minerals, including amphibole, lawsonite, chlorite, and serpentine; hydration of the ocean crust is typically fixed within a few million years of formation (5–6 wt.% H_2O; Alt and Teagle, 1999). Carbon is also fixed in the ocean crust through the flux of seawater and subsequent precipitation of carbonate in veins; the carbon content of the crust is highest at the top and decreases downward, and the crust continues to gain carbon throughout much of its transit across the ocean floor until it is insulated from fluid exposure through deposition of overlying sediments (Alt and Teagle, 1999). The oceanic crust is overlain by pelagic sediments whose lithology and composition (calcareous, siliceous or red clay) depend on the trajectory of the crust through the ocean basins. These sediment layers may be accreted upon subduction and do not necessarily reach sub-arc depths (von Huene and Scholl, 1991).

In a subduction zone, the negative buoyancy of the oceanic lithosphere (comprised of the mantle, oceanic crust, and pelagic sediments) drives its descent into the mantle. The time for the overlying mantle wedge to heat this cold lithosphere by conduction is longer than the rate of descent, producing an inverted temperature profile with a cool slab underlying a warm mantle wedge (Helffrich et al., 1989). As the descending slab is heated, temperature- and pressure-dependent metamorphic reactions occur, releasing significant proportions of the volatiles contained in the various layers of the oceanic lithosphere. The process of partially recycling carbon from the subducting slab is known as "decarbonation" ("devolatilization" for volatiles in general). The volatile flux from the descending slab into the overlying mantle wedge will lower the melting solidus, producing anatectic melts roughly at the nose of the 1300 °C isotherm (Grove et al., 2006; Schmidt and Poli, 1998). Driven by buoyancy forces, this volatile-rich melt rises via reactive porous flow and channel formation (Katz et al., 2003). During transport through the crust the (now partially fractionated) magma may acquire additional volatiles (and carbon) from crustal sources before eruption and degassing (Freda et al., 2008). The ultimate volcanic gas CO_2 flux from arc volcanoes is therefore controlled by the extent of devolatilization of the subducting slab and subsequent volatile delivery to the overlying mantle wedge. If significant amounts of volatiles from the oceanic lithosphere are lost before the slab reaches subarc depths, the subaerial CO_2 flux will be lower.

Thus, if we wish to understand the CO_2 flux out of arc volcanoes, we must constrain the limitations on devolatilization, particularly the depth of devolatilization. This is particularly important because, if the volatiles are released too early, they will migrate back to the ocean and will not emerge from subaerial volcanoes (termed 'forearc volatile release'). What controls decarbonation at 'sub-arc' depths? The extent of decarbonation is due largely to differences in thermal structure within the subduction zone, which is controlled by the following physical parameters (Kerrick and Connolly, 2001a,b; Peacock, 2003):

- Convergence rate
- Thermal structure of subducted lithosphere (function of plate age and sediment thickness)
- Geometry of the subduction zone
- Rate of shear heating

The mechanism (and precise metamorphic reactions) involved in volatile release during subduction largely relate to what is required to release water and carbon from the various hydroxylated and carbonate minerals in the various layers of the lithosphere. Kerrick and Connolly (2001a) calculated crustal decarbonation and dehydration extents by tracing the intersections of predetermined geotherms with phase equilibria computed for average CO_2-bearing oceanic metabasalts from Peacock and Wang (1999). The depths at which these continuous reactions occurred were found to be heavily dependent on the slab geotherm. However, decarbonation of the sediment layer was subsequently shown to be limited only to H_2O-rich sediments in high temperature geotherms and occurs at depths shallower than 80 km (Kerrick and Connolly, 2001b). This suggests that if significant decarbonation of the sedimentary and underlying crustal layers is to occur at sub-arc depths (where it can influence subaerial volcanic CO_2 fluxes), it must be induced by an alternative mechanism.

The extent of dehydration reactions at sub-arc depths is the critical factor controlling the decarbonation efficiency of subduction zones (Kerrick and Connolly, 2001a). When the temperature of the descending hydrated oceanic crust reaches ~500 °C, the transition to eclogite facies occurs, inducing the heterogeneous breakdown of the dominant hydrous minerals of lawsonite, chlorite and glaucophane to epidote, garnet and barrositic amphibole respectively (Liou et al., 1996; Schmidt and Poli, 1998). Depending on the slab geotherm,