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Geophysical and geochemical controls on abiotic carbon cycling on Earth-like planets

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A few solid exoplanets with possible surface liquid water [1] are promising targets to detect atmospheric spectral signs of life. This requires understanding background abiotic geological controls (outgassing, weathering) on atmospheric composition. Often, such controls are parameterized as lower boundary conditions [2], usually estimated from present Earth values [3]. However, outgassing likely depends on planet size [4], and surface sinks depend on the planet's bulk oxidation state, to which key species such as carbon are sensitive [2]. Here, we explore how size and redox affect geophysical and geochemical controls on abiotic cycling of carbon [5] on planets of similar insolation as Earth with rain. We treat the atmosphere and ocean as a single reservoir, understanding that larger ocean volumes can dissolve more gas. We find that the relative compositions of the surface and atmosphere, as well as the surface renewal rates, shape carbon abundance and speciation in the atmospheres of lifeless Earths.

1. Geochemical controls

On Earth, atmospheric carbon is transferred to the solid surface by weathering. A relevant reaction is $MgSiO_3 + CO_2(aq) = MgCO_3 + SiO_2$ [5]. The fluid-rock setting can be subaerial (continental weathering), or suboceanic (seafloor weathering). Reaction rates depend on temperature T via an Arrhenius law, the extent of chemical disequilibrium Ω (the ratio of reactant and product abundances to their values at equilibrium), pH, mineral surface properties, and the action of catalysts. Experimentally measured reaction rates are often fitted as [6]:

$$\frac{dm}{dt} = -\mathrm{SA}\ A\ e^{-\frac{E}{R(T-T_0)}}\ 10^{-(n\ pH)}\ (1-\Omega^p)^q \quad (1)$$

with m the moles of species per kg of water and SA the reacting surface area. The constant A and exponents n, p, and q are fitting parameters.

Abiotic carbon cycle models usually account for Ω and pH implicitly through power-law scalings to observed runoff and CO_2 partial pressure [3,5,7], ignoring surface composition and exposure rates. However, we find that weathering rates, computed with *PHREEQC* [6,8], depend more on Ω than T. In turn, Ω depends on the relative rates of rain (runoff) and unreacted surface exposure. If the former is slower, the surface is always fresh and the carbon drawdown flux is the product of the fluid delivery rate and its carbon content. For continental weathering, this is the limiting case of planets with little rain and no ocean. For seafloor weathering, this requires crustal recycling ($\sim 10^8$ year timescale on Earth) to be faster than fluid circulation ($\sim 10^3$ years on Earth). Thus, rock exposure is likely more limiting than water-rock reaction.

2. Geophysical controls

2.1. Crustal exposure

Continental physical and chemical weathering are both due in part to precipitation; thus their rates seem correlated [e.g. 9], yielding a partial reaction of 10-20% ($\Omega \sim 0.1$) for Si-, Al-rich crust and ~1% ($\Omega \sim 0.01$) for Mg-, Fe-rich crust. The related reaction timescale varies from years (felsic crust) to hours (mafic crust). With Earth-like runoff [3], fluxes of atmospheric carbon into the surface are a few nmol C m^{-2} s^{-1} at 25°C and 1 bar for both felsic and mafic crust (the latter reacts faster but is on average more reacted), comparable to previous estimates [3,5,7].

In seafloor weathering, the rate of ocean crust recycling depends on mantle convection (see 2.2). Only a small fraction of the crust reacts with seawater due to limited fractures from which circulating fluids can diffuse into the crust (at a rate of <20 m in the crust lifetime of 10^8 years [10]). Therefore, the flux of carbon taken up by seafloor crust is the fraction of initially dissolved carbon in seawater incorporated in the crust at chemical equilibrium, scaled by the mass of rock within diffusional reach of seawater.

2.2. Outgassing

Outgassing arises from melting of hot, low-pressure upwelled mantle material. The vigor of upwelling

likely peaks a few billion years into an Earth-sized planet's evolution. Outgassing also depends on the planet's tectonic mode, which ranges from stagnant-lid (as on Mars) to mobile-lid regimes (as on Earth). Mobile-lid convection occurs if plate yield stress (e.g. due to lithospheric weakening) is overcome by driving convective shear stresses at the base of the plate. This is less likely on larger planets ($> 1.5M_{\oplus}$), where yield stresses increase due to increased gravity (pressure) [11]. Convective driving stresses could increase with higher gravity (buoyancy forces), thickness of the convective layer, and thermal gradients across the mantle, but these effects are not as marked [11]. Larger planets also tend to be hotter and thus have higher viscosity contrasts, plus higher lower-mantle viscosities due to high ($> 10^{11}$ Pa) pressures at depth [12], which both decrease driving shear stresses [12,13]. Large, hot worlds may lose heat via increased mantle melting, magma transport through the stagnant lid, and surface hot spot volcanism [4,11], perhaps mitigated by higher melting temperatures for mantle material under higher lithospheric pressure [12]. Thus, mobile-lid Earth may be a high end-member of outgassing on solid worlds.

The species outgassed depend on source depth and magma composition [14]. The oxygen fugacity (redox state) of magmas could change by a factor $\lesssim 100$ upon ascent due to exsolution [14]. The redox of solar-system-like solid bodies outgassing is likely similar to Earth's over a range of sizes [15]. At 1573 K, CO_2 is the main outgassed species above a few bar, with H_2O dominating down to sub-mbar [15]. Thus, carbon release is more efficient if melting occurs deeper. For more reduced planets at 1 bar, the predominant carbon gases are instead CH_4 or, above 750 K, CO [16].

The carbon outgassing rate thus depends on magma generation rate (tectonic mode and convection vigor), magma volatile carbon abundance, and outgassing efficiency (depth). It is independent of rates of carbon subduction if the mantle holds enough carbon [7].

Acknowledgements

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