

Tracing whole-Earth carbon from the Hadean to present

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In response to the evolving thermal vigor and fugacity of oxygen and other volatiles, the behavior and fate of carbon and its partitioning between various layers of Earth - atmosphere, silicate Earth, and metallic core - varied through geologic time [1].

During the first few tens of millions of years of the Hadean Eon, carbon that participated in the core-forming, deep magma ocean, partitioned strongly into the metallic core. The Moon on the other hand, having a much shallower magma ocean likely held on to a large fraction of its bulk carbon. With almost all carbon of the chondritic building blocks being lost to space, restricted to nascent atmosphere, or sunk to the core, the silicate liquid mantle soon after core segregation was probably carbon-poor. Processes such as late bombardment of volatile-rich material, entrapped C-bearing metallic liquid in lower mantle solids, and ingassing from a C-rich atmosphere had opportunities to replenish mantle carbon by the end of the Hadean Eon. The crustal recycling zone temperature also likely was hotter until ~1.5 Ga; such slab thermal structure along with inconsistent subduction cycle might have hindered deep ingassing of surficial carbon. Massive release of CO₂ at the Archean and Paleoproterozoic volcanic arcs thus might have supplied the necessary dose of greenhouse gas in the atmosphere to offset the dimmer early Sun, sustaining liquid water on Earth's surface.

The P-T paths of subducting slabs of the Phanerozoic support transporting crustal carbonates past arc-magmatic depths, setting up systematic deep transfer of surficial carbon to the interior. Magmatic release of CO₂ balances the subduction input of carbonates and organic carbon. The proximal carrier-magma delivering mantle carbon to the exosphere depends chiefly on the thickness of the thermal boundary layer and mantle potential temperature - most strongly carbonated magma being the key agent beneath cratons, mildly carbonated magma for mature oceanic lithosphere, and basalts with trace amount of dissolved carbon beneath mid-oceanic ridges.

This talk will trace the origin of mantle carbon in the Earth-Moon system from the time of accretion, core formation, and magma ocean crystallization and will attempt developing a framework of carbon ingassing and outgassing fluxes in different time periods of whole Earth evolution.

[1] Dasgupta (2013), *RiMG* 75, 183-229.

Deep subduction of carbon and sulfur constrained by laboratory experiments

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The fate of volatile elements such as carbon and sulfur during subduction is critical because of their influence in a number of key aspects of planetary differentiation including partial melting, atmospheric chemistry and habitability, mobility and enrichment of ore forming metals, and redox evolution of the planetary interior. Yet, the efficiency of carbon and sulfur via subduction of crust is unresolved. Here we use phase equilibria experiments on carbonate-, sulfide-, and sulfate-bearing crust and sediments, plus experimental data and models of CO₂ and sulfur solubility in hydrous siliceous melt as a function of fO_2 to constrain the recycling efficiency of carbon and sulfur.

Carbon: Carbonate minerals are stable along P-T paths of most downgoing slabs and generation of carbonatitic melt is only possible for hot subductions and/or from deeply (>200 km) subducted sediments. In the absence of carbonate melting, transfer of carbon to sub-arc mantle is limited by solubility of CO₂ in rhyolitic melts. Experiments and thermodynamic modeling suggests that wt.% level CO₂ may be dissolved in rhyolitic melts generated by hydrous-fluid-fluxed melting of crust and sediments, with solubility diminishing with decreasing fO_2 in the presence of graphite. However, the extent of graphite and carbonate breakdown remains limited by the extent of hydrous melting, with the latter being controlled chiefly by bulk water content.

Sulfur: Sulfur content of downgoing crust is estimated to be lower than that of carbon, but sulfur content of pyrrhotite-saturated, slab melts is only ~100 ppm [1]. For anhydrite-saturated crust ($fO_2 > FMQ+3$), slab melts contain 1000s of ppm S, yet elimination of sulfate from slab requires large extent of slab melting and extensive flushing by hydrous fluids. With subducting slab being largely dehydrated approaching sub-arc depths, stability of sulfur-bearing phases in ocean crust is likely at all fO_2 . Further, sulfur addition to wedge mantle is most efficient via fluid addition (rather than melt) and fluids even at reduced conditions may be sufficiently rich in sulfur to elevate mantle wedge abundance.

Constraints on relative efficiency of deep subduction of carbon and sulfur will be presented and likely carrier of carbon versus sulfur to the arc source will be evaluated.

[1] Jégo & Dasgupta (2013), *GCA* 110, 106-134.