

Exchange of C between mantle and crust and its effect on global redox budgets

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Oxidation of earth's crust has been driven mainly by the carbon cycle, in which biological reduction of C is balanced by oxidation of Fe, S, or O (with H₂ often serving as an intermediate). Carbonate minerals in sediments and in weathered basalts are consistently enriched in ¹³C relative to the mantle. Since C is always being transferred from the mantle to the crust, that isotopic enrichment signals an equally continuous reduction of a portion of the incoming mantle CO₂. Accordingly, the release of oxidizing power by the carbon cycle has been continuous throughout earth history.

The rate at which oxidants are released will depend on (i) the rate at which C is delivered from the mantle, (ii) the fraction of C that is reduced and buried during each increment of geologic time, (iii) the rate at which C is returned to the mantle from the crust, and (iv) consumption of oxidants by recycling organic carbon. Inputs of mantle C were probably 10-fold higher at 4 Ga than at present [1]. Fractions of C reduced can be estimated from isotopic records of carbonates and organic matter. Crust-mantle carbon balances are unknown but illustrative cases can be examined.

If retention of C in the crust depends on the volume of continental crust and inventories thus grow slowly, release of oxidants will have been roughly linear from 4000 to 800 Ma. Between 800 Ma and the present, oxidants will have accumulated more rapidly, rising from 1200 to 1900 Emol O₂ equivalent. If the carbon-isotopic transients in the Paleoproterozoic truly represent organic-carbon burial events, the associated release of oxidizing power will have peaked at 1300 Emol O₂ equiv. at 2000 Ma, then declined until the Neoproterozoic.

If initial growth of the crustal inventory of C is rapid and the crust loses C to the mantle from 2500 Ma onward, the release of oxidants during the Archean will amount to half of the eventual total. During the Paleoproterozoic, the amount of carbon in play would be so large that the isotopic transients cannot be accepted as representing burial of organic carbon (they would call for hyperoxidation of the crust, substantially exceeding present levels).

The slow-growth cases are more consistent with organic geochemical and paleontological records. Better information about C budgets in subduction zones is required to judge their realism.

[1] Lowell, R. P. and Keller, S. M. (2003) *Geophys. Res. Ltrs.* **30**, 44.