

12.8 Weathering of Organic Carbon

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12.8.1 Introduction

In the earth sciences, weathering comprises the chemical and physical changes that occur on and near Earth's surface. Organic carbon weathering specifically involves those processes that affect sediment and rock reservoirs of organic carbon. During weathering, organic matter (OM) in sediment and rock reservoirs is subjected to loss through dissolution, erosion, and biological assimilation, and to transformations of chemical composition and physical structure. Some weathering processes lead to complete oxidation of OM to CO₂, while others transform highly reduced organic materials into more oxidized forms of OM, including incorporation into the biochemicals of living organisms. Weathering of OM is an important component of the geochemical carbon cycle. Oxidation of OM from rocks and sediments during weathering provides important controls on the O₂ and CO₂ concentrations in Earth's atmosphere over geologic time. Weathering of these rocks and sediments provides a source of many elements to natural waters and the oceans, important for understanding nutrient and other geochemical cycling. OM weathering also contributes carbon to heterotrophic microorganisms at the base of many aquatic food webs and serves as a source of OM-bound nutrients.

This chapter begins with a review of the major reservoirs and fluxes within the geochemical carbon cycle, estimates of the mass of the rock reservoir of organic carbon, and a global-scale view of major carbon fluxes. The chapter continues with a synthesis of field studies that explore the chemical transformations of OM within rock weathering profiles and other earth surface exposures of rock-derived OM. This is followed by examination of evidence for biological utilization of rock-derived OM during weathering, and examples of relict, rock-derived OM found in rivers and floodplain sediments. Global-scale estimates of carbon weathering are reviewed, obtained from numerical models of carbon cycling and from models of chemical weathering of sedimentary rocks. The chapter concludes with a synthesis of current understanding of organic carbon weathering and points to several key unknowns.

12.8.2 Reservoirs and Fluxes in the Geochemical Carbon Cycle

12.8.2.1 Rock Reservoirs of Carbon

Over 75 million petagrams (Pgs) of carbon are distributed among reservoirs of Earth's crust, oceans, atmosphere, and biosphere (1 Pg = 1 Gt = 10¹⁵ g) (Figure 1). Of this, the vast

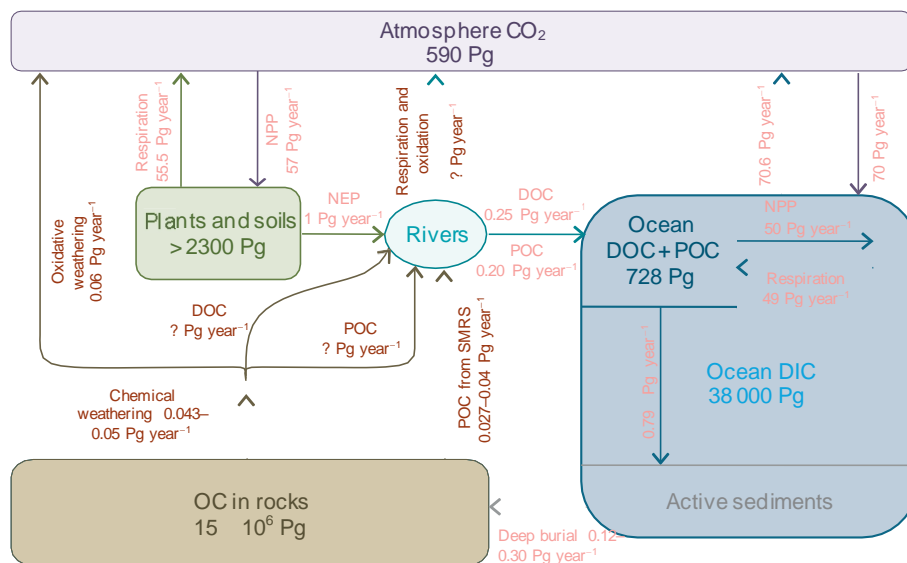


Figure 1 Integration of organic carbon weathering into the cycling of carbon through surficial and geologic reservoirs. Reservoir masses are in Pg, fluxes are in Pg year^{-1} . Values for NPP, respiration, and air-sea CO_2 exchange fluxes are from Sabine et al. (2004) and Sarmiento and Gruber (2006); NEP from Cole et al. (2007); river delivery of POC to oceans from Blair and Aller (2012); POC export to sediments from Dunne et al. (2007) and Burdige (2007); POC deep burial from Burdige (2007) and Blair and Aller (2012). Oxidative weathering of the rock reservoir of organic carbon releases approximately $0.06 \text{ Pg-C year}^{-1}$ as CO_2 . Rivers receive organic carbon from soils, terrestrial plants, and the chemical and physical weathering of ancient sedimentary rocks; estimates range from 0.07 to $0.09 \text{ Pg year}^{-1}$ of POC from the rock reservoir, with DOC contributions from the rock reservoir unknown. Estimates for global organic carbon burial rates range widely (see Burdige, 2007); here a value of $0.079 \text{ Pg year}^{-1}$ is used (Dunne et al., 2007); of this, much is remineralized in active sediments, with 0.12 – $0.3 \text{ Pg-C year}^{-1}$ reintroduced to the rock reservoir of organic carbon below the zone of active diagenesis (Blair and Aller, 2012; Burdige, 2007). Diagram design courtesy of J. Kocis.

majority is found in rock reservoirs in the form of either inorganic carbon (i.e., carbonate minerals such as calcite and dolomite) or organic carbon (i.e., solvent-insoluble, macromolecular carbon termed kerogen). Inorganic carbon represents chemical and mineral species in which all carbon atoms are fully oxidized. Organic carbon is more chemically diverse, with innumerable carbon-bearing materials found in biological and geological reservoirs. All of these, however, are characterized by electron-rich chemically reduced carbon susceptible to oxidation to inorganic carbon.

The rock reservoirs of carbon include approximately 60 million Pg of inorganic carbon and 15 million Pg of organic carbon. Of this organic carbon, the majority occurs in sedimentary rocks in the form of solid-phase, macromolecular OM termed kerogen. Although kerogen can be highly concentrated in some rocks, such as coals, which can be almost 100% OM, and organic-rich black shales, which can be 5–10% organic carbon by weight or even higher, most organic carbon in sedimentary rocks is present at very low concentrations much less than 1% organic carbon by weight (Bernier and Canfield, 1989; Raiswell and Berner, 1986; Ronov, 1976; Turekian and Wedepohl, 1961). Other forms of reduced carbon in rock reservoirs include graphite, which is a highly condensed polyaromatic mineral that forms during metamorphism of OM-bearing sedimentary rocks; polyaromatic transitional forms between kerogen and graphite, also formed during metamorphism; black carbon, which is also a highly condensed polyaromatic material that formed during incomplete combustion of vegetation over geologic history, and more recently through incomplete combustion of fossil fuels; and bitumen, which is

liquid or gaseous solvent-soluble OM that includes fossil fuels such as petroleum and natural gas. Fossil fuels are estimated to comprise much less than 1% of total crustal organic carbon.

As seen in Figure 1, the mass of organic carbon in crustal rocks ($15 \times 10^6 \text{ Pg}$) dwarfs all other organic carbon reservoirs combined. There are several thousand Pg of organic carbon in soils worldwide (Sabine et al., 2004), although more recent estimates of high-latitude peatlands suggest that polar peatlands and permafrost may contain at least 1600 Pg of organic carbon (Tarnocai et al., 2009) and that the total global soil carbon reserve ($\sim 2300 \text{ Pg}$) has been underestimated. Terrestrial vegetation comprises 650 Pg of organic carbon. In the oceans, organic carbon occurs in dissolved form (DOC – dissolved organic carbon, 725 Pg of carbon) and particulate form (POC – particulate organic carbon, 3 Pg of carbon). Reduced carbon gases in the atmosphere, such as CH_4 , contribute less than 0.005 Pg to total global carbon stocks. Together, the global mass of organic carbon not in rock reservoirs is only 0.02–0.04% of the mass of the rock reservoir of organic carbon; essentially all organic carbon on Earth is in rocks and sediments.

12.8.2.2 Addition of OM to the Rock Reservoir: OM Burial

Organic carbon is delivered to the rock reservoir through burial in sediments. Primary production of the terrestrial and marine biosphere generates 105 Pg year^{-1} of new organic carbon. Most of this carbon is rapidly oxidized to inorganic carbon in the water column of oceans, rivers, and lakes, with less than 0.5% being delivered to sediments (Burdige, 2007; Hedges and

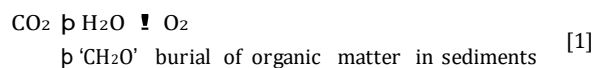
Keil, 1995). The flux of organic carbon delivery to sediments is poorly quantified, with estimates in the literature ranging over an order of magnitude from 0.16 to 2.5 Pg-C year⁻¹ (summarized by Burdige, 2007; see also Dunne et al., 2007). Within sediments, aerobic and anaerobic heterotrophic processes further degrade and oxidize sedimentary OM, a process called remineralization, such that only a small flux of carbon is ultimately incorporated into the rock reservoir. This flux too is poorly constrained, with rates of 0.12–0.3 Pg year⁻¹ commonly cited (Burdige, 2007; Hedges and Keil, 1995). One result of this slow burial flux relative to the size of the organic carbon rock reservoir is that the rock reservoir of organic carbon exhibits a residence time of millions of years. Using the carbon burial estimate of 0.16 Pg C year⁻¹ from Hedges and Keil (1995) and a mass of organic carbon in the rock reservoir of 15 million Pg-C gives a residence time of almost 100 Ma. This is likely an underestimate, as this burial flux does not account for gradual degradation of OM in biologically active deep sediments, and thus it overestimates actual accumulation of organic carbon into rock reservoirs. Nor does this calculation account for organic carbon losses from sediments and sedimentary rocks during deep diagenesis, thermal maturation, and metamorphism. Estimates of incorporation of organic carbon into the rock reservoir based on isotope mass balance model of the geochemical carbon cycle (discussed below) suggest an oxidative weathering flux ranging between 0.05 and 0.1 Pg year⁻¹, and a true residence time for rock reservoir organic carbon of several hundred million years.

Burial of organic carbon is not uniformly distributed around the globe, but is highly focused in nearshore environments along continental margins (Bernier, 1982, 1989; Blair and Aller, 2012; Burdige, 2007; Dunne et al., 2007). This is summarized in Figure 2, which demonstrates that while the open oceans (89% of ocean surface area) account for 80% of primary production and 69% of carbon export from surface waters but less than 2% of organic carbon burial, nearshore shelf environments that are only 5% of global ocean surface area account for 85% of global organic carbon burial. Within the broad category of nearshore, river-dominated shelves, OM preservation and burial efficiency are greatest

along active continental margins, where rivers drain uplands with little to no lowland storage in floodplains or deltas, in part due to the highly episodic nature of discharge events and delivery of OM to the deep ocean (Blair and Aller, 2012). In contrast, deltas and nearshore environments with long particle residence times prior to export to the deep ocean, and thus long cumulative exposure to dissolved O₂, serve as 'efficient incinerators' of OM with relatively poor OM burial efficiency (Blair and Aller, 2012). These factors are important not only for establishing global carbon budgets but also for understanding geographic patterns of carbon weathering, as the uplift and erosion of sedimentary rocks from different depositional settings will result in very different potentials for carbon weathering.

12.8.2.3 Removal of OM from the Rock Reservoir: Weathering, Erosion, and Oxidation

Addition of organic carbon into the rock reservoir is believed to match the flux of oxidative weathering of rock OM into inorganic carbon. This balance is represented by the equations:



Note that in these equations, CH₂O is not meant to indicate a particular organic compound (i.e., formaldehyde) but rather a representative composition of sedimentary OM. Over geologic time, burial of OM equates to long-term release of O₂ to Earth's atmosphere. Burial in this context means incorporation of OM into the rock reservoir following respiration and other degradation processes during burial and diagenesis; this is, as a matter of course, a smaller flux than the annual delivery of OM to sediments, as much OM degradation occurs in active sediments. This release is countered by consumption of O₂ during OM weathering.

The balance between these two reactions controls the size of the rock reservoir of organic carbon and also contributes to

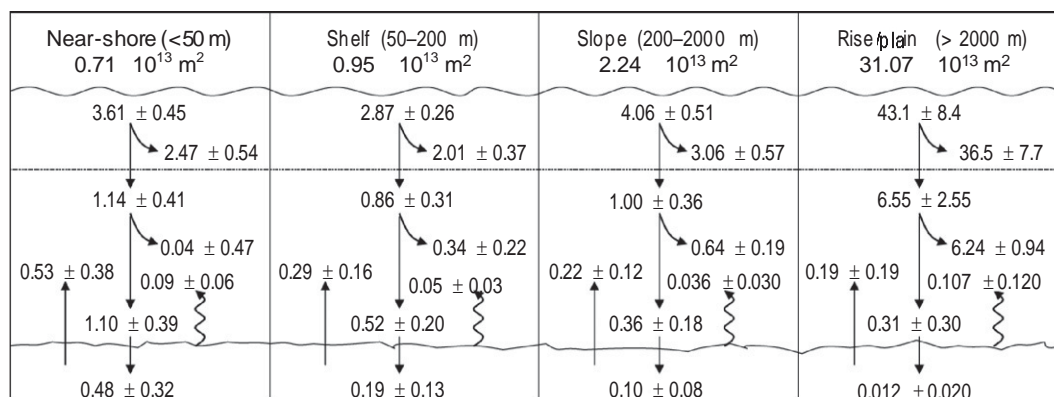


Figure 2 Global particulate organic carbon export and cycling, from Dunne et al. (2007). Calculations are based on satellite-derived primary production and models of particle sinking and remineralization rates and sediment accumulation. Locations of organic carbon product, export, and burial are separated into nearshore, shelf, slope and rise plain environments. All fluxes are in units of Pg-C year⁻¹. Down arrows indicate organic carbon fluxes, up arrows and curved arrows indicate mineralization (carbon oxidation) fluxes, and squiggly arrows indicate dissolved organic carbon fluxes. This analysis highlights the importance of nearshore and shelf environments in global burial of organic carbon.

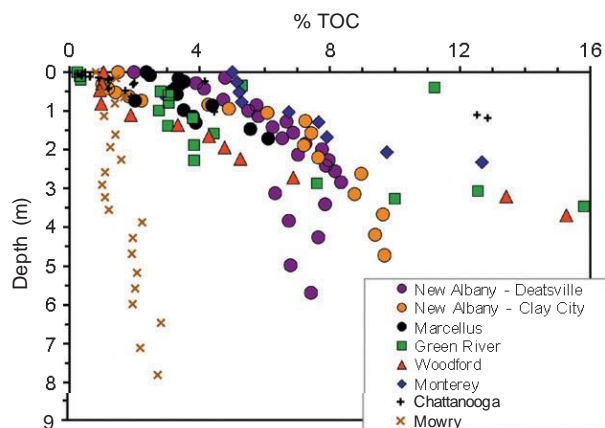


Figure 3 Decrease in organic carbon content (% TOC) in weathering profiles developed on OM-rich shales. Organic carbon weight percent was measured along individual beds of each weathering profile. Depth is distance in meters normal to the surface, calculated from the dip angle of each bed and the slope of the land surface. Data are from [Petsch \(2000\)](#) and [Petsch et al. \(2000\)](#).

controls of the concentration of O_2 and CO_2 in the atmosphere (see [Chapter 10.11](#) for full discussion of the global oxygen cycle). This control on atmospheric composition provides strong justification that global organic carbon burial rates are matched by oxidative weathering fluxes; without a near balance over geologic time, both the O_2 composition of the atmosphere and $\delta^{13}C$ values of reservoirs of the global carbon cycle would exhibit imbalance and trends through time not observed in the rock record ([Bergman et al., 2004](#); [Berner, 1987, 1989, 2006](#); [Garrels and Lerman, 1984](#); [Kump and Arthur, 1999](#); [Kump and Garrels, 1986](#); [Lasaga, 1989](#); [Petsch and Berner, 1998](#)). Small imbalances between the fluxes of oxidative weathering of rock organic carbon and incorporation of organic carbon into the rock reservoir on the order of 0.01 – 0.04 $Pg\ year^{-1}$ (averaged over millions of years) are recorded in the isotopic composition of carbonate rocks over geologic time; model estimates suggest that over Phanerozoic time OC burial fluxes have ranged between 0.01 and 0.07 $Pg\ year^{-1}$ while oxidative weathering of OM has ranged between 0.05 and 0.07 $Pg\ year^{-1}$ ([Berner, 1989, 2003](#); [Petsch, 2000](#)). This oxidative weathering flux is a much smaller flux of inorganic carbon to the Earth's surface than fluxes such as global respiration (~ 100 $Pg\ year^{-1}$), air–sea CO_2 exchange (~ 70 $Pg\ year^{-1}$), or even anthropogenic CO_2 release through fossil fuel combustion, recently estimated at greater than 7 $Pg\ year^{-1}$. The model estimate of global rock-derived organic carbon oxidation remains to be validated in studies that rely on direct measurement of carbon fluxes from active sites of carbon weathering ([Figure 3](#)).

12.8.3 Weathering of Kerogen

12.8.3.1 Weathering of Kerogen in Black Shales

12.8.3.1.1 Decreases in organic carbon content

Kerogen is commonly defined as the solvent-insoluble macromolecular OM found in sedimentary rocks. [Vandenbroucke and Largeau \(2007\)](#) provide a recent review of evolution,

origin, and structure of this material that comprises the largest single mass of organic carbon on the Earth. In particular, both the chemical composition (large, diverse, and complex, macromolecular materials with far fewer reactive heteroatomic moieties than found in biological OM) and the physical presentation (largely hydrophobic, tightly associated with a mineral matrix, and largely resistant to low-temperature or aqueous chemical reaction) would suggest a material that is inert to most geochemical reactions and processes. Nonetheless, both geochemical carbon cycle modeling exercises (described above) and field and laboratory studies indicate that kerogen does participate in global carbon cycling.

It has long been recognized that rock weathering leads to changes in the abundance of OM within sedimentary rocks exposed at Earth's surface including black shales ([Clayton and Swetland, 1978](#); [Lewan, 1980](#); [Leythauser, 1973](#); [Littke et al., 1991](#); [Petsch et al., 2000](#); [Wildman et al., 2004](#)) and coals ([Lo and Cardott, 1995](#); [Nip et al., 1989](#)). [Leythauser \(1973\)](#) showed a 25% loss of organic carbon content in surface-weathered samples of Mancos Shale compared to unweathered samples. Clayton and Swetland examined natural weathering in the OM-rich Phosphoria Formation (Permian, UT, USA) and the OM-lean Pierre Shale (Upper Cretaceous, CO, USA). While core samples of unweathered Phosphoria Fm. contained between 2% and 4% organic carbon by weight, weathered samples in the upper meter of the core ranged between 0.99% and 1.38% organic carbon, and outcrop samples contained only approximately 0.6% organic carbon. No trends in organic carbon content were observed in the Pierre Shale, with all samples from outcrop to 6.7 m depth exhibiting similarly low concentrations of organic carbon (0.75–0.97%). In a study of weathering at a surface exposure of the Upper McAlester Coal (Middle Pennsylvanian, Oklahoma, USA), [Lo and Cardott \(1995\)](#) found a decrease from 69.3% organic carbon at depth to 50.5% organic carbon in shallow samples; an unknown amount of soil had been removed from this site prior to study. [Copard et al. \(2002\)](#) compared weathered and unweathered samples of coal from the Ales coalfield (France) and found substantial alteration of both physical and chemical characteristics of the weathered coal. In particular, a loss of total organic carbon and an increase in Rock-Eval T_{max} and oxygen index (OI) values were found. [Lo and Cardott \(1995\)](#) also examined a weathering profile of the Woodford Shale (Late Devonian, Oklahoma, USA) but found no systematic decrease in organic carbon content within the 5 m profile. [Petsch \(2000\)](#) and [Petsch et al. \(2000\)](#) examined weathering of OM-rich black shales at nine sites across the United States, including two exposures of the Monterey Shale (Miocene, California), the Green River Shale (Eocene, Utah), the Mowry Shale (Cretaceous, Utah), Marcellus Shale (Middle Devonian, New York), the Woodford Shale (Late Devonian, Oklahoma), the Chattanooga Shale (Late Devonian, Tennessee), and two exposures of New Albany Shale (Late Devonian, Kentucky). This study showed decreased organic carbon content within individual shale strata upon weathering, showing that differences in organic carbon content did not result from bed-to-bed heterogeneity but rather from weathering ([Figure 3](#)). In slowly eroding landscapes with modest relief, such as exposures of the New Albany, Woodford, and Marcellus Shales, organic carbon loss can penetrate several meters into the rock, while in more

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