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Marine dissolved organic carbon (DOC) is a large (660 Pg C) reactive carbon reservoir that mediates the oceanic microbial food web and interacts with climate on both short and long timescales. Carbon isotopic content provides information on the DOC source via δ13C and age via Δ14C. Bulk isotope measurements suggest a microbially sourced DOC reservoir with two distinct components of differing radiocarbon age. However, such measurements cannot determine internal dynamics and fluxes. Here we analyze serial oxidation experiments to quantify the isotopic diversity of DOC at an oligotrophic site in the central Pacific Ocean. Our results show diversity in both stable and radio isotopes at all depths, confirming DOC cycling hidden within bulk analyses. We confirm the presence of isotopically enriched, modern DOC cocycling with an isotopically depleted older fraction in the upper ocean. However, our results show that up to 30% of the deep DOC reservoir is modern and supported by a 1 Pg C/yr carbon flux, which is 10 times higher than inferred from bulk isotope measurements. Isotopically depleted material turns over at an apparent time scale of 30,000 yr, which is far slower than indicated by bulk isotope measurements. These results are consistent with global DOC measurements and explain both the fluctuations in deep DOC concentration and the anomalous radiocarbon values of DOC in the Southern Ocean. Collectively these results provide an unprecedented view of the ways in which DOC moves through the marine carbon cycle.

Radiocarbon is a natural tracer of carbon flow through dissolved organic carbon (DOC) (1). As plankton grow and are consumed by grazers, organic matter with a modern radiocarbon value (Δ14C = −50‰) is released into surface waters where it accumulates as semilabile DOC (2–4). Semilabile DOC undergoes net remineralization below the euphotic zone and gradually diminishes in concentration with depth to approximately 1,000 m, below which it appears to vanish. Oceanic profiles of total DOC and DOC radiocarbon (DOCΔ14C) are therefore characterized by high values (60–80 μM carbon; −200‰ to −400‰) in surface waters and lower values at depth (35–40 μM; −400‰ to −550‰) (2). The −200‰ to −300‰ depletion in DOCΔ14C values in surface seawater relative to semilabile DOCΔ14C indicates the presence of a second refractory DOC fraction with an old radiocarbon age. The inverse proportionality between DOC concentration and radiocarbon value in depth profiles suggests that refractory DOC is well mixed throughout the entire water column (2, 3, 5, 6). The origin of the refractory DOC fraction is obscure, but stable isotopes (δ13C) show little change with depth δ13C = −21.7‰ to −20.2‰ (2, 7–9), indicating a common, autochthonous planktonic source for both fractions (2).

DOC and DOCΔ14C profiles can be reproduced in a simple two-component model (TCM) that includes a variable amount of semilabile DOC cycling in the upper ocean (<1,000 m) superimposed on a ubiquitous background of radiocarbon-depleted refractory DOC (2, 3). In the TCM, semilabile DOC cycles on timescales of months to years, whereas refractory DOC cycles over several millennia (2, 3, 10). The TCM provides an excellent 1D representation of DOC and isotope values in seawater.

The simple mixing of two isotopically distinct components implicit in the TCM can be contrasted with the wide range of mass fluxes and isotope values measured in potential sources of marine DOC. These sources include terrestrial organic matter from C3 and C4 plants delivered by rivers (1, 4, 11), chemosynthetic organic matter from hydrothermal vent systems (12), organic matter derived from the oxidation of sedimentary methane (13), atmospheric deposition of black carbon from fossil fuel and biomass burning (14, 15), chemosynthetic carbon as Earth's atmosphere, yet its cycling timescales and composition remain poorly constrained. We use serial oxidation experiments to measure the quantitative distribution of carbon isotopes inside the DOC reservoir, allowing us to estimate both its cycling timescales and source distribution. We find that a large portion of deep water DOC has a modern radiocarbon age and a fast turnover time supported by particle dissolution. In addition, stable carbon isotopes allow for diverse sources of carbon, besides microbial production, to quantitatively feed this reservoir. Our work suggests a DOC cycle that is far more intricate, and potentially variable on shorter timescales, than previously envisioned.


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few exceptions (20, 23) conclude that the TCM is sufficient to explain their data. The discrepancy between the isotopic diversity in DOC sources and the narrow isotopic range of bulk DOC measurements has two resolutions. Either significant cycling of DOC is hidden by the TCM or many of these sources do not accumulate within the marine DOC reservoir. This paper provides a means for evaluating these two distinct hypotheses.

**Materials and Methods**

Samples were collected in July 2010 from Station ALOHA (22° 45’N; 158°W), site of the Hawaii Ocean Time-series (HOT) program. Whole seawater was frozen and returned to the National Ocean Sciences Accelerator Mass Spectrometer facility in Woods Hole, MA, for processing. Stepwise oxidation was performed using radiocarbon clean procedures on a customized, large volume UV apparatus. The total mass and mean isotopic value of DOC in surface, mid-depth, and deep seawater agrees with earlier results from a remote site in the North Pacific Subtropical Gyre (NPSG) used to establish the TCM (2, 3). The 100% depletion in our surface water $\Delta^{14}C$ value, relative to those measured two decades ago, is due to the location of station ALOHA on the southern flank of the NPSG and the slow removal of bomb radiocarbon (radiocarbon produced during atmospheric testing of nuclear weapons) from the surface ocean over the last two decades (24). Further details can be found in SI Materials and Methods.

To estimate the isotopic distributions of components within DOC and quantify carbon fluxes that may be obscured by the TCM, we used the stepwise oxidation of DOC under high-intensity UV light (25, 26). Our experimental approach is not designed to mimic natural photo-oxidative processes. Rather, we use photo-oxidation as a tool to generate an isotopic time series of DOC components from which we derive evidence for a distribution of isotopic abundances among the components of DOC. Carbon from components that are readily oxidized by UV light will appear early in the time series, whereas carbon from components resistant to UV light will appear later, as oxidation proceeds to completion. The approach is analogous to using chemical oxidation techniques to remove a specific chemical fraction (22) or to using spatial gradients to infer internal distributions (5). These time series were modeled in terms of parallel first-order reactions to estimate the radiocarbon distribution (SI Materials and Methods and SI Text).

**The Isotope Time Series**

Fig. 1 shows the serial oxidation time series for our samples (numeric values in SI Text) and includes concentration, $\delta^{13}C$, $\delta^{14}C$, and $\Delta^{14}C$. We use $\delta^{13}C$ in our analysis rather than $\Delta^{14}C$ because our methods require linear isotope units. It should, however, be noted that the $\Delta^{14}C$ and the $\delta^{14}C$ time series are similar, with the only substantial deviation being the final time point. $\Delta^{14}C$ was calculated using the $\delta^{13}C$ and separately measured $\delta^{13}C$ values. Time points were chosen to minimize mass differences between each fraction to equalize statistical errors and keep mass-dependent errors systematic (25). Mass values were blank corrected by subtracting the amount of carbon recovered at each time point from a separate time series using previously UV-oxidized seawater.

The structure of the isotope time series provides direct information on the isotopic composition of DOC. The $\delta^{13}C$ time series has two local minima at all three depths suggesting at least three distinct $\delta^{13}C$ fractions. One minimum occurs after approximately 5 min of total oxidation time (see data in SI Text to resolve early times), whereas the other occurs after nearly 90 min. The strong enrichment in $\delta^{13}C$ values at the final time point results from isotopic fractionation during UV oxidation, with measured fractionation factors for small organic compounds being as great as $100\%\delta^{13}C$ (27). If this fractionation is taken into account, the intrinsic isotopic variations underlying the fluctuations at all three depths must still be at least $100\%\delta^{13}C$. Taking into account the attenuation caused by mixing of multiple components, this range allows for significant contributions to deep water DOC from terrestrial organic matter, black carbon, hydrothermal vents, and methane seeps. Exceptionally efficient sinks for these external sources of carbon are not required.

Fractionation is less relevant for $\delta^{14}C$ as the dynamic range is 10 times larger than for $\delta^{13}C$. For the $\delta^{14}C$ time series, the local extremal values, along with the decreasing trend, also suggest three isotopic groups with a minimal spread of 150$\%\delta^{14}C$, 120$\%\delta^{14}C$, and 100$\%\delta^{14}C$ for the surface, mid-depth, and deep water, respectively. However, the large changes in $\Delta^{14}C$ (Fig. 1D) over relatively short periods of time suggest DOC components with a much larger isotopic range. To estimate the full radiocarbon range, we require a kinetic model for oxidation under UV light.

**Modeling the Radiocarbon Distribution**

The oxidation of DOC by UV light has been modeled as both a parallel first-order (25) and second-order kinetic process (26). For parallel first-order processes, the initial oxidation rate will scale linearly with DOC concentration, whereas second-order kinetics predicts that the initial decay rate scales quadratically with DOC concentration. To directly test the kinetic form, we...
performed serial oxidation experiments under multiple dilutions of filtered Woods Hole seawater and showed that the initial decay rate scales linearly with concentration (28). Therefore, DOC photo-oxidation in our high-intensity apparatus is best described by parallel first-order kinetics rather than second-order kinetics (26) (SI Text).

To estimate the isotopic values of the different DOC components, we therefore represent the oxidation progression as a superposition of parallel first-order reactions (29)

$$g_i(t) = \int_{-\infty}^{\infty} \rho_i(k)e^{-kt}dk.$$  \hspace{1cm} [1]

The function $g_i(t)$ is the amount of $i$ C, where $i = \text{carbon isotope } 12, 13, \text{or} 14$, remaining in the DOC sample after a time $t$; and $\rho_i(k)$ is the amount of $i$ C associated with a first-order rate constant between $k$ and $k + dk$. After correcting for isotopic fractionation, the relevant isotopic ratios are $R(k) = \rho_i(k)/\rho_{i2}(k)$. The isotopic ratios $R(k)$ along with the concentration as a function of rate constant $\rho_{i2}(k)$ allow us to estimate the distribution of isotopic values. This estimate is made by matching concentrations with isotopic ratios through their common rate constants.

To render the problem numerically tractable, we approximate the integral as a sum of $n$ discrete components

$$g_i(t) = \sum_{j=1}^{n} \rho_{ij}e^{-a_jt},$$ \hspace{1cm} [2]

where the doubly subscripted $a_j$ and $\rho_{ij}$ are the fractionation factor and initial concentration, respectively, of the $j^{th}$ component of C. We solve for the parameter values that minimize the error between our model and the serial oxidation data. Independent of fractionation, each inflection point in the isotope time series suggests an additional required component, leading to six (three each from the inflection points in the $\delta^{13}C$ and $\delta^{14}C$ time series). We thus compute the best fit solution using six exponential components, constraining the solution to fall within measured isotopic values of marine organic matter at each depth ($-1000‰ ≤ \delta^{13}C ≤ 150‰; -40‰ ≤ \delta^{14}C ≤ -10‰$). Unlike earlier radiocarbon mixing models, which assume end member values or infer them from plots, the approach taken here is to let all of the parameters vary until an optimal fit to the concentration, $\delta^{13}C$, and $\delta^{14}C$ time series is obtained. As high-parameter, nonlinear fits are sensitive to noise, we use a Monte-Carlo approach, repeating the procedure on many (1,000) realizations of the data by perturbing the original data with random error and look for general patterns in isotope space for all 1,000 sets of mass and isotope pairs (6,000 pairs). The mass estimates are not tied to the number of exponential components used in the fitting procedure. The ensuing mass and DOC$^{14}C$ values were grouped into modern ($\delta^{14}C ≥ -50‰$), depleted ($-600‰ ≤ \delta^{13}C < -50‰$), and highly depleted ($\delta^{13}C < -600‰$) fractions. The estimated isotope distributions (Fig. 2) show the average concentration density (micromoles of DOC per liter of seawater divided by the isotope range of each interval) estimate within each fraction. The concentration of DOC in each of the three fractions is equal to the area under each bar in Fig. 2 (value in micromol given above each bar). Further technical details can be found in SI Text.

DOC$^{14}C$ for all samples includes modern ($>-50‰$), depleted ($-50‰ ≤ \delta^{13}C < -600‰$), and highly depleted ($< -600‰$) DOC, where $-600‰$ is the lowest radiocarbon value found in deep Pacific water. The broad range ($-1000‰$ to $-50‰$) of DOC$^{14}C$ values for the depleted and highly depleted DOC suggests a wide range of turnover times for these fractions. Surface seawater at Station ALOHA contains approximately 29 M radiocarbon modern DOC, which decreases in concentration to 15 M at 500 m and 9 M at 2,000 m. The high relative abundance ($\sim 40%$ total DOC) and enriched isotope values of modern DOC limits the resolution of depleted and highly depleted fractions in our surface and mid-depth samples. The higher total amount of depleted and highly depleted carbon at the surface ($\sim 47 M$) relative to 500 and 2,000 m ($\sim 36$ and 31 M, respectively) could be due in part to inputs of depleted atmospheric and riverine carbon, but is most likely due to limitations in the resolution of isotope space for all 1,000 sets of mass and isotope pairs (6,000 pairs). The mass estimates are not tied to the number of exponential components used in the fitting procedure. The ensuing mass and DOC$^{14}C$ values were grouped into modern ($\delta^{14}C ≥ -50‰$), depleted ($-600‰ ≤ \delta^{13}C < -50‰$), and highly depleted ($\delta^{13}C < -600‰$) fractions. The estimated isotope distributions (Fig. 2) show the average concentration density (micromoles of DOC per liter of seawater divided by the isotope range of each interval) estimate within each fraction. The concentration of DOC in each of the three fractions is equal to the area under each bar in Fig. 2 (value in micromol given above each bar). Further technical details can be found in SI Text.

[Fig. 2. Radiocarbon composition of DOC, expressed as a scaled probability distribution. The estimated isotopic distributions for 50- (A), 500- (B), and 2,000-m (C) depths. The area under each bar corresponds to the average concentration of the modern ($\delta^{14}C ≥ -50‰$), depleted ($-600‰ ≤ \delta^{13}C < -50‰$), and highly depleted ($\delta^{13}C < -600‰$) fractions. Error bars are the 16% and 84% percentiles of our estimate for that fraction. Bold values above each bar are the concentration (µM) values (area of each bar). For example, our plot for 2,000 m suggests that approximately 24 µM is highly depleted, 7 µM is depleted, and 9 µM modern organic carbon make up DOC at that depth.]

radiocarbon modern material to the deep ocean (17). Global shallow export production estimated from sediment trap measurements and ocean models is approximately 11 Pg C/y, with between 2.3 and 5.5 Pg C/y falling through 500 m (30, 31). The modern radiocarbon value of \(\sim 10\ \mu M\) of deep DOC suggests that this material has a turnover timescale less than 50 y and is thus semilabile. If deep, semilabile DOC is in a steady state governed by first-order kinetics, at least 1 Pg C/y flows through this fraction. Our measurements therefore suggest that 20–50% of sinking particulate organic matter is solubilized during export and sequestered for decadal timescales as semilabile DOC within the deep ocean. The carbon flux through deep semilabile DOC is one to two orders of magnitude higher than the flux through DOC calculated from bulk radiocarbon values and dominates the carbon flux through deep sea DOC.

The depleted DOC fraction would include contributions from in situ chemoheterotrophy, chemolithotrophy (16, 20, 32), and the advection of DOC from higher latitudes (33–35). It is also likely that some modern and highly depleted carbon is not fully resolved in our measurements and therefore contributes to the depleted fraction. Highly depleted DOC is near 25 \(\mu M\) and \(-800\%o\) at 2,000 m. This fraction is significantly depleted relative to the mean \(\Delta^{14}C\) value for DOC in the deep ocean (−800‰ vs. −522‰, respectively) (2), suggesting a radiocarbon age near 12,000 y. Current models suggest that this refractory portion of DOC survives multiple ocean mixing cycles and is in an approximate steady state with modern inputs.

In this case, it is important to realize that the radiocarbon age does not equate to the mean age of the DOC. When a reservoir containing a single component with turnover time \(\tau\) is in steady state, its mean age equals its turnover time, and the age distribution is exponential (36). Similar reasoning leads to the following relationship between the radiocarbon age \(a_r\) of the reservoir and its turnover time \(\tau\) (SI Text)

\[
\tau = \frac{\ln 2}{\lambda}.
\]

where \(\lambda\) is the decay constant of radiocarbon. Inserting \(a_r = 12,000\) y, we calculate the turnover time \(\tau\) to be 30,000 y for refractory DOC. This time scale suggests either DOC cycling takes much longer than the currently believed 6,000 y (3) or that an external source of isotopically depleted (pre-aged and potentially labile) carbon supports the refractory DOC.

**Global Context**

The current form of the TCM is sufficient to explain many open ocean DOC measurements. Chief among its accomplishments are an explanation for the depleted radiocarbon values found in surface ocean DOC and the slow decrease in DOC concentration between the deep North Atlantic and Pacific Oceans. The fundamental tenet of the TCM, that radiocarbon-depleted DOC persists throughout the water column, is well supported by our data. However, certain measurements remain hard to explain unless one allows for a semilabile reservoir of DOC in the deep ocean.

DOC concentrations in the deep ocean for a nominal global ocean transit (Fig. 4) show a general decrease consistent with the slow decay models used to explain them (33). These models use a superposition of material with different first-order decay rates to explain the slowdown of net DOC degradation in the ocean. Decay in these model systems is completely monotonic and fails...
Changes in DOC concentration (micromoles per kilogram). DOC (34) < 25 μM and in the Circumpolar Deep Water along Pacific transect P16 (*). Water samples were used from the neutral density surfaces consistent with these water masses: 41.25 < ρ<sub>9000</sub> < 41.5 in the Atlantic and 45.85 < ρ<sub>9000</sub> in the Pacific (34). The running mean across 15° N-S (solid line) is superimposed on the individual DOC measurements (single points). The 1- to 2-μM increase in DOC at the equator relative to the background trend in both basins is consistent with increased particle export from enhanced primary production at the equator. Data from cdiac.esd.ornl.gov/oceans/RepeatSections/.

Fig. 4. Changes in DOC concentration (micromoles per kilogram). DOC (34) in the core of the North Atlantic Deep Water along Atlantic transect A16 (*) and in the Circumpolar Deep Water along Pacific transect P16 (*). Water samples were used from the neutral density surfaces consistent with these water masses: 41.25 < ρ<sub>9000</sub> < 41.5 in the Atlantic and 45.85 < ρ<sub>9000</sub> in the Pacific (34). The running mean across 15° N-S (solid line) is superimposed on the individual DOC measurements (single points). The 1- to 2-μM increase in DOC at the equator relative to the background trend in both basins is consistent with increased particle export from enhanced primary production at the equator. Data from cdiac.esd.ornl.gov/oceans/RepeatSections/.

to accommodate increases in either bulk DOC concentration or decay rate. Deep ocean export of particulate organic carbon (POC) into the DOC reservoir predicts that in areas of high export production there should be local elevations in deep sea DOC concentrations due to a larger reservoir of semilabile DOC. Global DOC data plotted along density surfaces (34) as it travels from the North Atlantic to the North Pacific Ocean (Fig. 4) provide evidence for these systematic fluctuations. In equatorial regions and the Southern Ocean, we find increases in DOC concentration of 1–2 μM or 10–20% of the semilabile reservoir. Post-nuclear bomb testing radiocarbon values for the deep semilabile reservoir of DOC suggest a turnover time of <50 y for this portion. Any large impulse of semilabile DOC should thus persist over 15°-20° N-S based on a mean drift in the deep ocean of 0.3°-0.4° per year, which is consistent with the observed spatial fluctuations in deep DOC concentrations (Fig. 4). A recent reanalysis of deep Pacific data provides additional evidence that loss of refractory DOC is not a gradual, monotonic process but is localized to mid-depth regions in the North and South Pacific basins (37). Spatial differences in deep transport or release of semilabile DOC could result in the lowered observed DOC concentrations in these regions.

A continual supply of semilabile DOC into the deep ocean from the sinking of large particles should also drive regional fluctuations in deep DOCΔ14C values. The turnover time of semilabile DOC in surface waters is short relative to radioactive decay so that semilabile DOCΔ14C ≈ DICΔ14C. DICΔ14C values can therefore be used as a proxy for semilabile DOCΔ14C (2, 8). Large latitudinal changes in surface water DICΔ14C (and hence semilabile DOCΔ14C) (1) should affect deep sea DOCΔ14C values as semilabile organic matter is cycled through the deep DOC reservoir. This effect should be especially clear as one travels from the Sargasso Sea, through the Southern Ocean, and into the North Central Pacific. Along this journey, surface DIC ranges from Δ14C ~ 50‰ to 150‰ in the North Atlantic to Δ14C ~ −100‰ to 0‰ in the Southern Ocean and Δ14C ~ 0‰ to 150‰ in the North Pacific (38). Assuming an average background concentration of refractory DOC at ~25 μM and ~ −80‰ in the Sargasso Sea, ~ −100‰ in the Southern Ocean, and ~140‰ in the North Central Pacific, consistent with measured surface DICΔ14C values and trends.

If DOC conservatively ages in the deep ocean, its radiocarbon age and that of DIC should change at the same rate. A plot of mean radiocarbon ages of deep water DOC and DIC (Fig. 5) in the Sargasso Sea (2), Southern Ocean (23), and North Central Pacific Ocean (2) shows that, although radiocarbon values in the North Pacific are consistent with conservative aging, the DOC in the Southern Ocean is 500–1,500 y too old (23). Compared with DIC, DOC ages more rapidly as water moves from the North Atlantic to the Southern Ocean and then more slowly as water moves from the Southern Ocean into the North Pacific (23). These trends are straightforwardly explained if semilabile DOC in the deep Sargasso Sea is replaced by surface derived, isotopically depleted, semilabile DOC in the Southern Ocean (more rapid apparent aging of DOC) and then replaced again by modern DOC in the deep North Pacific (slower apparent aging of DOC).

The current paradigm of DOC cycling assumes that the dynamics of DOC in the deep ocean are advectively controlled; that once photosynthetically derived DOC is exported from the surface, it undergoes purely degradative processes (33, 34). This assumption allows one to calculate the net DOC flux from deep concentration gradients and equate it with the gross carbon flux (33, 34). If the dissolution of POC supports a large, semilabile portion of deep DOC, however, then the gross flux is no longer calculable from deep sea gradients in DOC. Under this scenario, the dynamics of deep ocean DOC is affected by surface processes like primary and export production. In this case, the flux through the reservoir could be substantially higher. Regional changes in the global DOC concentration and radiocarbon data support this perspective.

Carbon flux from POC to DOC could provide a unifying framework for DOC cycling in disparate environments. POC-DOC transfer from terrestrial sources are believed to affect the bulk DOCΔ14C values in the Mid-Atlantic bight, Western North Pacific, and Arctic Ocean (7, 20, 39). Griffith et al. (20) used isotopic evidence to suggest that 30% of deep DOC in Canada Basin water could be terrestrially derived, which would leave the background, refractory, marine-derived DOC fraction at...
a concentration of 28 μM, well below DOC values in the deep North Pacific but similar to the values determined by our measurements. This amount of background carbon requires that deep Pacific DOC (35–40 μM) contains 7–12 μM semilabile DOC. The Mediterranean Sea may also be unified within the poc-DOC framework. Although the turnover time for Mediterranean deep water is an order of magnitude less than in the global ocean (100s vs. 1,000s of years), deep DOC values reach those found in the North Central Pacific (40).

Unique decay conditions may be present. However, low DOC values are consistent with the ultra-oligotrophic surface conditions and low inputs of deep semilabile DOC from particles (41).

Conclusion

The contrast between the large number of diverse sources that supply carbon to marine DOC and the isotopic uniformity measured in stable and radiocarbon analyses and inferred from the TCM has long been considered as a paradox in ocean carbon cycling. Our results show that marine DOC is isotopically diverse, with a broad range of potential sources and cycling timescales. Deep DOC δ13C has a range of at least 10‰, allowing for significant contributions from terrestrial organic matter, black carbon, DOC from hydrothermal sources, and methane seeps. Exceptionally efficient sinks for these external sources of carbon do not need to be invoked to explain the isotopic value of DOC in the deep sea. Furthermore, we suggest that the total flux of carbon through DOC in the deep ocean is at least an order of magnitude higher than the net carbon flux derived from abyssal concentration gradients (33) and bulk radiocarbon measurements (3). Current flux estimates that equate total flux with net flux assume that inputs from the dissolution of sinking particles and chemooautotrophy are small. Our data suggest otherwise. Active cycling of carbon and large annual carbon fluxes through DOC are not restricted to the surface ocean but occur throughout the water column (Fig. 3). Our work suggests a DOC cycle that is far more intricate, and potentially variable on shorter timescales, than previously envisioned.

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