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Chemosynthetic origin of ^{14}C -depleted dissolved organic matter in a ridge-flank hydrothermal system

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Hydrothermal fluids circulate through extensive areas of the upper oceanic crust. Most hydrothermal circulation occurs on ridge flanks^{1,2}, where low-temperature fluids flow through porous basalts. These fluids contain variable levels of dissolved organic carbon, but the source and composition of this carbon are uncertain. Here, we report $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ measurements of dissolved organic carbon in ridge-flank and on-axis hydrothermal fluids sampled from the Juan de Fuca Ridge. Dissolved organic carbon from two independent ridge-flank sites was characterized by low $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ values. The $\delta^{13}\text{C}$ values ranged from -26 to -35‰ , and were consistent with a chemoautotrophic origin. The ^{14}C ages of the dissolved organic carbon ranged from 11,800 to 14,400 years before present, revealing that the carbon was around three times older than dissolved organics in the deep ocean. The $\Delta^{14}\text{C}$ values of the ridge-flank dissolved organic matter also corresponded closely to those of dissolved inorganic carbon in the same fluid samples. Taken together, the data suggest that chemosynthetic crustal microbial communities synthesize dissolved organic carbon from inorganic carbon in ridge-flank fluids. We suggest that ridge-flank circulation may support an indigenous biosphere extensive enough to export substantial fixed carbon, with distinct isotopic and probably compositional character, to the overlying ocean.

Circulation of hydrothermal fluids in upper oceanic crust may support one of the most extensive, but least understood, of the Earth's biogeochemical systems. However, little is known about non-living organic matter carried in crustal hydrothermal fluids or its possible impact on the carbon cycle of the overlying ocean. Elevated concentrations of particulate organic carbon with distinct composition are present near venting sites³, but particulate organic carbon composes only a small fraction of organic matter in most natural waters, with dissolved organic carbon (DOC) making up most of it⁴. Particulate organic carbon is typically both more labile and surface-active than DOC, so that particle compositions tend to reflect local conditions and relatively short-timescale processes⁵. DOC probably represents most organic matter carried by crustal fluids and subsequently vented to the overlying ocean, with its chemical and isotopic composition providing an integrated view of sources and processes remote from local venting sites.

Although high-temperature systems at the mid-ocean ridges are better studied, growing evidence indicates that, globally, most hydrothermal circulation occurs instead in lower-temperature fluids on ridge flanks^{1,2}. In the Juan de Fuca Ridge (JDFR) flank region that we sampled, such fluids contain low total DOC concentrations ($\sim 10\text{--}15\ \mu\text{M}$; ref. 6). These values suggest that much oceanic DOC must be removed during the long crustal fluid residence times ($\sim 10,000$ yr; ref. 7), either by microbial utilization or abiotic adsorption⁶. However, concentration data carry no information regarding the source or composition of the DOC in vented fluids. If vented material were residual deep-ocean DOC, this would indicate a heterotrophic system with respect to dissolved organics, and potential impacts on the oceanic reservoir could be limited. In contrast, if a substantial portion of vented ridge-flank DOC were autochthonous, with distinct isotopic or biochemical composition, then even small inputs could represent an important unrecognized source of fixed carbon to the overlying ocean DOC pool.

We measured coupled stable carbon ($\delta^{13}\text{C}$) and radiocarbon ($\Delta^{14}\text{C}$) isotopic compositions of ultrafiltered DOC (UDOC) isolated from both ridge-flank and selected on-axis low-temperature fluid sources on the JDFR system (Fig. 1; Supplementary Methods). Our ridge-flank sites are located approximately 100 km east of the ridge axis on 3.5-Myr-old crust, and include a venting outcrop (Baby Bare) sampled by stainless-steel probes driven directly into rock⁸, and also an Ocean Drilling Program borehole (Hole 1026B, freely venting at the time of sampling) accessing basement fluid. Hydrologic and chemical data indicate ridge-flank fluid circulation here is independent from on-axis circulation⁹; thus, DOC in these fluids is not directly linked to high-temperature circulation or axial hydrology or processes.

Ridge-flank UDOC concentrations ($1.2\text{--}1.4\ \mu\text{M}$) were low, consistent with total DOC data⁶, whereas UDOC concentrations at lower-temperature axial sites ($6\text{--}11\ \mu\text{M}$) were more similar to background sea water ($6.8\ \mu\text{M}$; Table 1). The offset between on-axis and ridge-flank values is consistent with total DOC concentrations⁶, and also with the large background seawater admixture expected at on-axis lower-temperature sites (Supplementary Methods). Background seawater UDOC properties, including overall UDOC recovery ($6.8\ \mu\text{M}$), and isotopic values ($\delta^{13}\text{C}$, -21.1‰ ; $\Delta^{14}\text{C}$, -443‰), very closely matched values expected for total DOC from

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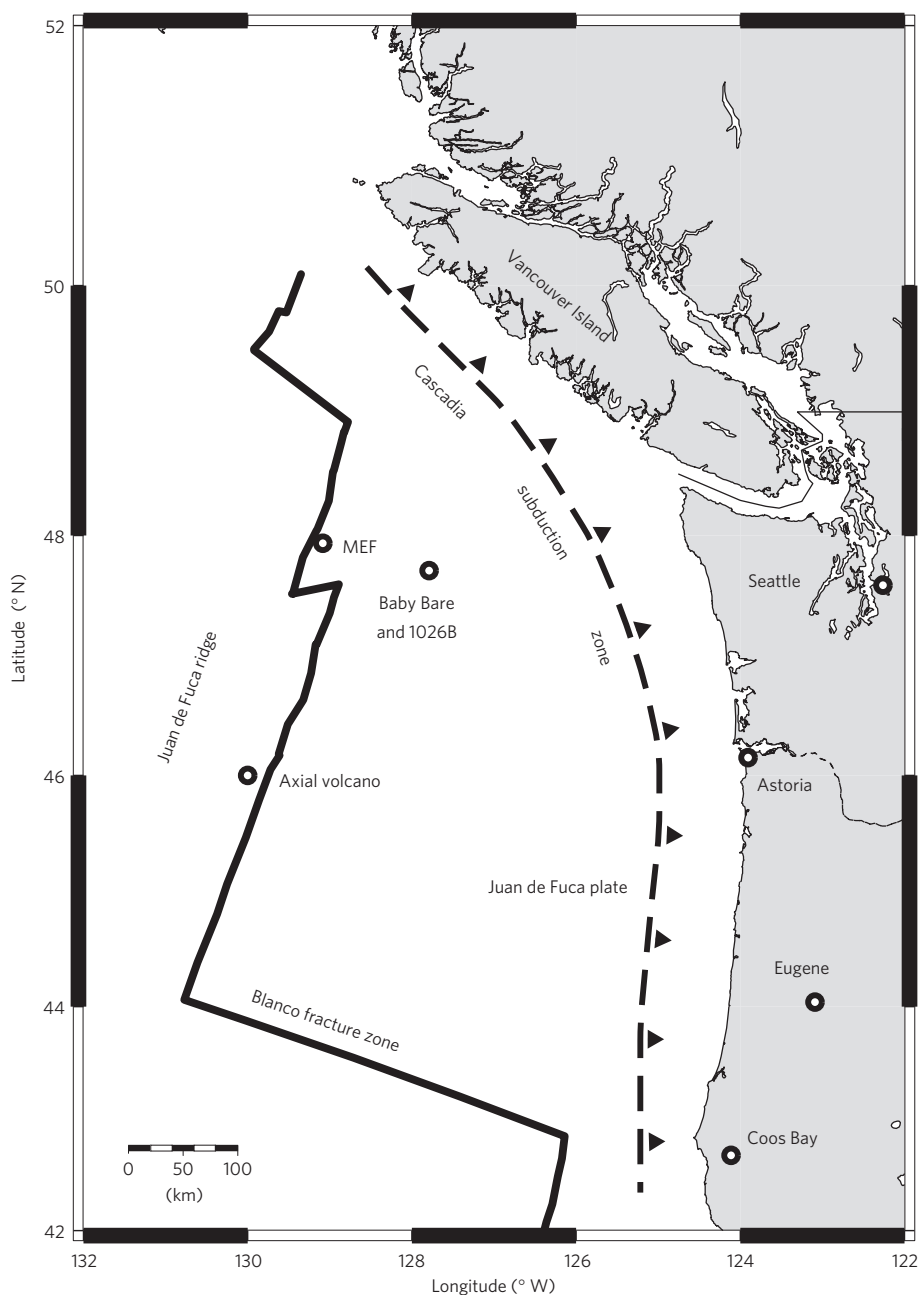


Figure 1 | Sampling locations on JDFR spreading centre. Ridge-flank sites (Baby Bare seamount and Ocean Drilling Program Hole 1026B) are located within sedimented, 3.5-Myr-old crust approximately 100 km from the ridge axis in Cascadia Basin. These sites are separated by 7 km, but are indicated together owing to map scale. The on-axis sites are geographically distant, with Easter Island and West Grotto located on the Main Endeavor Field (MEF), and Axial volcano several hundred kilometres to the south.

the deep Pacific Ocean^{5,10}, and indicate no substantial effects from our isolation protocols on isotopic values.

Both stable and radiocarbon values from the on-axis fluids showed clear, but small, offsets versus background seawater UDOC (Table 1). The $\delta^{13}\text{C}$ values for on-axis fluids are slightly higher relative to seawater UDOC, whereas $\Delta^{14}\text{C}$ values are lower (Fig. 2a,b; Table 1). This suggests the addition of locally produced DOC, however superimposed on a much larger background of deep-ocean material. This is consistent with total DOC data⁶ and also expected hydrodynamics: on-axis lower-temperature fluids are variable mixtures of entrained local sea water and high-temperature fluid^{7,11}. Broader sampling of on-axis lower-temperature fluids at the JDFR has indicated that although DOC concentrations are variable, on average these fluids represent a net DOC source⁶. Our results are

consistent with this picture, because on-axis lower-temperature DOC composition at any specific site would be expected to reflect mixtures between background seawater organics (always quantitatively dominant) and variable amounts of added material.

In contrast, at ridge-flank sites, $\delta^{13}\text{C}$ values are sharply offset from seawater values (Fig. 2). The $\delta^{13}\text{C}$ values are both much lower (-26 and -35‰) relative to either seawater DOC or surface-derived marine organic carbon (-21 to -22‰). These values are similar to those characteristic of chemoautotrophic organic matter in modern and ancient environments^{12,13}, and also many groups of chemoautotrophic microorganisms¹⁴. Autotrophic microbial $\delta^{13}\text{C}$ values should derive from both fluid dissolved inorganic carbon (DIC) $\delta^{13}\text{C}$ and subsequent autotrophic fractionation. When depleted DIC $\delta^{13}\text{C}$ values in these fluids are taken into account

Table 1 | Sample data and isotopic compositions.

Sample Year	Sea water		Ridge-flank				On-axis					
	2,540 m CTD 2002	1026B 2002	BB-P4 2003	Axial 2002	Easter Island 2002	West Grotto 2003						
Temperature (°C)	1.9	63	21	40	23	25						
UDOC (μM)	6.8	1.2	1.4	6.0	5.8	10.6						
DOC (μM)	38	14	11*	35	44	39						
AMS ID	CAMS—105887 ±	UC—25218 ±	UC—25219 ±	UC—25216 ±	UC—25217 ±	UC—25215 ±						
δ ¹³ C (‰)	−21.1	0.2	−26.1	2	−34.5	2	−18.6	2	−19.4	2	−18.4	2
Δ ¹⁴ C (‰)	−442.7	2.5	−771.5	2.0	−834.9	4.3	−521.6	1.5	−487.6	1.9	−454.0	1.2
FM	0.5600	0.0025	0.2300	0.0020	0.1662	0.0043	0.4814	0.0015	0.5157	0.0019	0.5495	0.0012
Age (yr BP)	4,690	40	11,810	70	14,420	210	5,870	30	5,320	30	4,810	20

UDOC concentrations are calculated on the basis of total carbon recovered and volume sampled. The errors for isotopic values are propagated AMS errors (calculations outlined in the Methods section, and in more detail in Supplementary Methods). The total DOC concentration (flagged by *) was determined independently on the same fluids, with values previously published⁶. One DOC value (Baby Bare BB-P4, 2003 cruise) was not available, and a 2002 value for the same fluid source is included. Where replicate samples from the same site were analysed, the average value is given. CTD = conductivity-temperature-depth; FM = fraction modern.

(−6.5 to −9.5‰; ref. 7), the observed UDOC values correspond well with fractionation ranges expected from a number of cultured free-living chemoautotrophs¹⁴ (Supplementary Discussion). Furthermore, the more depleted UDOC δ¹³C at Baby Bare is also consistent with the offset in DIC δ¹³C between the two sites⁷, as would be expected for chemosynthetic production. However, significant variation in chemosynthetic fractionations¹⁴, coupled with probably diverse microbial sources and crustal habitats associated with these systems^{8,15}, suggests caution in attempting to interpret δ¹³C values in terms of any specific organisms.

Ridge-flank UDOC Δ¹⁴C values for Baby Bare and Hole 1026B samples are also much lower (−772 and −835‰ respectively), relative to both local deep-seawater UDOC (−443‰; Table 1), and total DOC anywhere in the world ocean^{5,16}. If the dominant UDOC source were chemoautotrophy, then Δ¹⁴C values for organic matter would also be expected to be similar to Δ¹⁴C of the DIC in the same fluids. In fact, UDOC Δ¹⁴C values correspond very closely with fluid DIC Δ¹⁴C (ref. 7; Fig. 2b). Although radioactive decay of ¹⁴C in entrained seawater DOC could also produce older DOC, this would not influence stable carbon isotopes, and thus could not explain the depleted δ¹³C values. Taken together, the chemoautotrophic δ¹³C values and close correspondence between Δ¹⁴C values of UDOC and local DIC strongly support the conclusion that dissolved organics vented are autochthonous, synthesized *de novo* by microbial communities in the crust.

There are also alternative environmental interpretations that might be considered for these data, such as selective degradation of oceanic DOC, and sedimentary or terrestrial influences. For example, as total DOC concentrations are low, highly selective degradation of ocean DOC might potentially alter the isotopic value of remaining material. However, isotopic change with DOC degradation is not observed in the overlying ocean⁵, suggesting this as unlikely. Furthermore, the operational lipid fraction is the only component having strongly offset ¹³C and ¹⁴C values versus total UDOC¹⁷, but this is present in only trace amounts (0.3% or less¹⁷), and so could not explain our results through selective concentration. UDOC samples in fresh water can also have low δ¹³C values¹⁸; however, terrestrial contribution to deep-Pacific dissolved organic matter is also trace¹⁹, and background Cascadia Basin UDOC (−21.1‰) bulk isotopic values suggest no significant terrestrial component. Sediments are another potential organic-matter source, because inorganic fluid composition has suggested some sedimentary influence in JDFR^{20,21}. Radioactive decay of organic ¹⁴C in sediments also would result in lower

Δ¹⁴C organic matter; however, in this case δ¹³C values would remain similar to overlying primary production that created them (∼−21 to −22‰ in this region²²). In particular, nearby sediment porewater DOC maintains very similar values down to near basement (−20 to −22‰; ref. 23), inconsistent with a sedimentary explanation. Finally, abiotic organic-carbon synthesis has also been suggested in the JDFR system¹⁵, representing an alternative carbon source possibly consistent with both δ¹³C and Δ¹⁴C values. Although a major abiotic contribution seems unlikely (and any low-molecular-weight products from Fischer-Tropsch synthesis would not be retained in our high-molecular-weight samples), such compounds could comprise an electron and carbon source for chemolithotrophic bacteria^{15,24,25}. This pathway would not fundamentally change our interpretation (because the abiotic organic matter would also have the Δ¹⁴C of its source DIC pool), but it would add an important mechanistic step between fluid DIC, microbial biomass and high-molecular-weight DOC, and could also contribute to low δ¹³C values²⁶. Further detail on these alternative scenarios is given in the Supplementary Discussion.

Together, these data indicate that DOC vented from lower-temperature ridge-flank regions can represent an unrecognized source of DOC to the subsurface ocean. In particular, the material we measured (at 11,400–14,000 ¹⁴C yr BP) is 2.5–3 times older than deep-ocean DOC. Although DOC concentrations across different crustal environments may vary widely²⁴, any organic carbon ultimately derived from crustal DIC would necessarily represent an analogous source of ¹⁴C-depleted DOC to the deep sea. These observations pose the question of possible influence on the deep ocean's DOC reservoir, in particular because low Δ¹⁴C values are a central observation for interpreting its character and cycling^{5,16}. Globally, fluid flux from lower-temperature ridge-flank hydrothermal systems is far higher than axial venting, and may approach total riverine input to the world ocean¹². However, as few DOC studies are available, it is difficult to quantitatively assess possible carbon fluxes. Nevertheless, if one assumes a total ridge-flank fluid input to the world ocean between $4.8 \times 10^{12} \text{ m}^3 \text{ yr}^{-1}$ (ref. 1) and $2.1 \times 10^{13} \text{ m}^3 \text{ yr}^{-1}$ (ref. 2), and an average DOC concentration of 20 μM, then approximately 1.2 to $5 \times 10^{12} \text{ g C yr}^{-1}$ of carbon would be added to the deep ocean, or ∼1–5% of the steady-state input of DOC to the global deep ocean ($6 \times 10^{17} \text{ g C/6000 } ^{14}\text{C yr}$; ref. 16). If the near-quantitative removal of ocean DOC during circulation that our data implies were also typical, the ultimate effect would also increase owing to the simultaneous removal of original deep-ocean material.

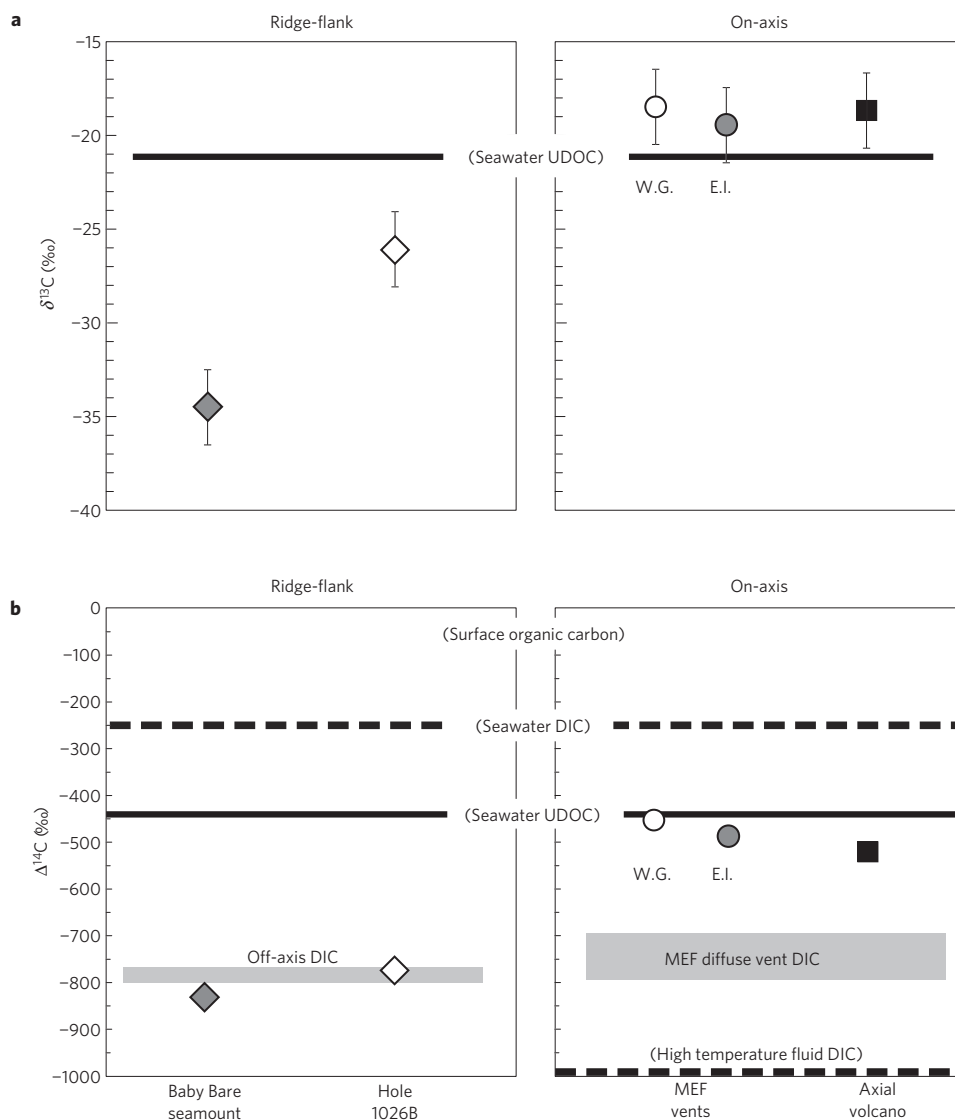


Figure 2 | Carbon isotopic composition of UDOC from low-temperature hydrothermal fluids. In ridge-flank fluids, low $\delta^{13}\text{C}$ values (**a**), together with close correspondence between UDOC and coexisting DIC $\Delta^{14}\text{C}$ (**b**), indicate a chemoautotrophic source for DOC vented to the ocean. On-axis isotopic values also suggest some autochthonous input, but also that fluids are dominated by mixing with deep sea water. The dashed and solid lines in both panels indicate $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ endmembers of different ocean carbon sources. The shaded areas (in **b**) indicate DIC $\Delta^{14}\text{C}$ value ranges in the same hydrothermal fluids⁷. The error bars in **a** are AMS-derived $\delta^{13}\text{C}$ errors (in **b**, the errors are smaller than the symbols). E.I. = Easter Island; W.G. = West Grotto. The sample sites and other abbreviations are as in Fig. 1.

Although such contributions may seem relatively small, it is the very low $\Delta^{14}\text{C}$ signature, in combination with recent recognition of the varied and dynamic nature of the deep-ocean DOC reservoir, that may be most important. Recent work showing widely different $\Delta^{14}\text{C}$ values for specific DOC biochemical classes has been interpreted to indicate a spectrum of cycling rates¹⁷, but also suggests that vented low- $\Delta^{14}\text{C}$ material with distinct composition could disproportionately influence individual DOC subcomponents in the deep sea. However, an important overall caveat is that the ultimate contribution to the deep-ocean reservoir will depend strongly on the relative residence time of vented organics. This is well illustrated by considering riverine DOC: its contribution to the total deep-ocean DOC pool is minor (probably owing to relatively rapid photochemical/microbial degradation²⁷), despite having a global input sufficient to support all subsurface DOC turnover⁴. If the vented material is more refractory than average deep-ocean dissolved organic matter, it could in fact build up to comprise a greater proportion than the 1–5% input

estimate would imply, potentially biasing our view of deep DOC recalcitrance; however, if degraded rapidly once in the deep ocean, then the ultimate influence might be small or negligible. At present, as neither composition nor relative persistence of vented material is known, it is not possible to clearly assess quantitative significance.

Ultimately, the central implication of these data may be that ridge-flank circulation can not only support an indigenous biosphere, but one expansive enough to export substantial fixed carbon to the overlying ocean. Together, our data suggest that vented DOC from this system is almost entirely synthesized by autotrophic bacteria. Earlier work indicated the presence of thermophilic chemoautotrophic microbial strains at these sites^{8,15}; however, the low DOC concentrations alone suggested that ridge-flank circulation acts mainly as a carbon sink⁶. In contrast, our isotopic and concentration data indicate that over the multi-millennial timescales of ridge-flank circulation⁷, deep-ocean DOC is largely removed, and replaced with new material having very different isotopic, and probably compositional, character. This interpretation is strongly

supported by a growing amount of literature demonstrating a widely distributed deep microbial biosphere with surprisingly diverse metabolic capabilities^{23,28,29}, as well as the expected efficient degradation of DOC during long-term circulation over microbial-covered surfaces (Supplementary Discussion). Recent data demonstrating chemoautotrophic bacterial populations supported directly by basalt–seawater chemical reactions²⁸ may be particularly relevant to this system, because the energy potential from this mechanism alone may be able to support a biosphere on par with the entire overlying ocean²⁹. The overall impact of many ridge-flank systems may thus be to simultaneously act as a ‘scrubber’ for surface-derived organic carbon, and a source of new, chemosynthetic material. Understanding the ultimate impacts on oceanic biogeochemical cycles will require determining the chemical composition and reactivity of crustal fluid DOC, coupled with broader global sampling.

Methods

Fluids were obtained from a variety of hydrothermal sources using methods adapted for each site, including stainless-steel probes driven into the exposed rock outcrop at Baby Bare, direct sampling of the over-pressured Hole 1026B, and specialized sampling devices for on-axis diffuse fluid vents. Oceanic water samples were also collected using conductivity–temperature–depth casts in Cascadia Basin (2,540 m depth) far from ridge influence, and isolated UDOC was used as our background seawater reference. Large volume crustal fluid samples were recovered from the sea floor using a custom-built large-volume elevator sampler, and inorganic composition data indicated that the off-axis samples we obtained were highly pure crustal fluid (Supplementary Methods). Furthermore, fluids in the passive-intake sampler design contacted only Tedlar bags and Teflon tubing, which were acid-cleaned and rinsed with Milli-Q water before each deployment. Tedlar sample bags treated with this cleaning protocol were tested before cruises and found to contribute no detectable DOC (ref. 6). Samples for total DOC measurements were also collected by collaborators from the identical fluid sources, using a small-volume sampler employing the same sample bags⁶. To isolate sufficient DOC for $\Delta^{14}\text{C}$ analyses, tangential flow ultrafiltration was used to concentrate the ultrafiltered higher-molecular-weight fraction of DOC (UDOC; 0.1 μM –1,000 D). UDOC subsamples were diluted to ~1 litre with pre-irradiated purified Milli-Q water, and quantitatively oxidized to CO_2 with a mercury arc lamp photochemical reactor system for ^{14}C analysis³⁰. Accelerator mass spectrometry (AMS) measurements were made at UCI Keck Carbon Cycle Accelerator Mass Spectrometry facility. All isotopic measurements were blank-corrected for graphitization and AMS analysis, and also corrected with error propagation for the ultraviolet-extraction procedural blank. Further details on sampling, DOC isolation and AMS measurements are provided in Supplementary Methods.

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Author contributions

M.D.M. planned the project, supervised sampling and analyses, analysed data and wrote the paper; B.D.W. designed and carried out UDOC isolations and sample processing, analysed and plotted data. I.V. designed sampling and ultrafiltration equipment, carried out UDOC isolations and assisted with sample processing. S.R.B. carried out ^{14}C -UDOC sample analyses and analysed data. T.P.G. and E.R.M.D. supervised ^{14}C sample analyses and interpreted data.

Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper on www.nature.com/naturegeoscience. Reprints and permissions information is available online at <http://npg.nature.com/reprintsandpermissions>. Correspondence and requests for materials should be addressed to M.D.M.