Hadal aragonite records venting of stagnant paleoseawater in the hydrated forearc mantle

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The hadal zone at trenches is a unique region where forearc mantle rocks are directly exposed at the ocean floor owing to tectonic erosion. Circulation of seawater in the mantle rock induces carbonate precipitation within the deep-sea forearc mantle, but the timescale and rates of the circulation are unclear. Here we investigated a peculiar occurrence of calcium carbonate (aragonite) in forearc mantle rocks recovered from ~6400 m water depth in the Izu-Ogasawara Trench. On the basis of microtextures, strontium-carbon-oxygen isotope geochemistry, and radiocarbon analysis, we found that the aragonite is sourced from seawater that accumulated for more than 42,000 years. Aragonite precipitation is triggered by episodic rupture events that expel the accumulated fluids at 10^{-2} – 10^{-1} m s⁻¹ and which continue for a few decades at most. We suggest that the recycling of subducted seawater from the shallowest forearc mantle influences carbon transport from the surface to Earth's interior.

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The hadal zone is one of the least explored territories on Earth's surface and is characterized by high hydrostatic pressures, geological instability, and low nutrient supply. In particular, as the depth of a trench is greater than the thickness of arc crust, fresh mantle rocks are continuously exposed at erosive trenches¹. Chemical reactions between mantle rocks and seawater exert an influence on global elemental transport and energy production for life^{2–7}. Life in the hadal zone is potentially fed by the energy released during the alteration of mantle rocks (i.e., serpentinization)⁸, which produces an alkaline (pH = 9–11), reducing, and hydrogen- and methane-rich fluid derived from circulating seawater^{2,3}. Understanding the mechanism and dynamics of coupled fluid flow, mass transport, and reaction provides a quantitative understanding of the link between the lithosphere and biosphere.

Carbonate minerals provide a unique opportunity to investigate the effects of fluids on the carbon cycle^{9–13}, which occurs actively in subduction zones^{14–18}. Carbon is released from the subducting slab via metamorphic devolatilization and melting, and is returned to Earth's surface via plumes emitted from volcanoes and through diffuse degassing from the flanks of volcanoes. The deep carbon cycle (>70 km depth) occurs on timescales of around 10 Myr,^{15,17,19} however, carbon cycling also occurs in the shallow forearc (<20 km). Investigation of upwelling fluids and serpentinite from the Mariana forearc has revealed that carbon is released from the subducting slab at shallow forearc depths^{20–22}. However, in contrast to the deep carbon cycle, little is known about the timescale and rates of carbon and fluid cycling in shallower forearc regions.

Aragonite (CaCO₃), a polymorph of calcite, has been identified in samples of serpentinized peridotite recovered from the seafloor^{13,23–26}. In the ocean, the chemical environments for inorganic aragonite precipitation are limited by the aragonite saturation depth (ASD), which is defined by the thermodynamic equilibrium between aragonite and seawater. The ASD varies substantially with latitude and longitude and is estimated to be ~2500 and 0–1000 m below sea level (mbsl) in the North Atlantic and North Pacific oceans, respectively²⁷. In hydrothermal vents along the Mid Atlantic Ridge (MAR), aragonite precipitation occurs at depths of 2000–2500 mbsl, which is slightly shallower than the ASD^{28,29}. Aragonite precipitation can also occur at depths greater than the ASD^{23,24,26,30,31}, where it is induced by the interaction between ultramafic rocks and circulating seawater^{13,23}. Here we report a new occurrence of aragonite in serpentinized peridotite recovered from a depth of >6400 mbsl from the inner wall of the Izu–Ogasawara Trench (IOT; Fig. 1a, b). This aragonite is from the hadal zone (>6000 mbsl), which is far deeper than the ASD (1000 mbsl)²⁷, aragonite compensation depth (ACD; 500–1500 mbsl)³², and carbonate (calcite) compensation depth (CCD; 4500 mbsl;³³ Fig. 1c), suggesting that the aragonite was formed by fluid–rock reactions. Therefore, the hadal aragonite potentially records fluid flow and chemical reactions during the circulation of seawater within the shallowest parts of the forearc mantle, and its investigation should provide insights into the transport of carbon from the surface to Earth's interior. For this study, we used major- and trace-element compositions, C–O–Sr isotopes, and microstructural characteristics of hadal aragonite to determine the origin of carbonic fluids and mechanisms of aragonite formation. Moreover, we used radiocarbon dating to estimate fluid residence time in the hydrothermal system^{34,35}. Combining the results of these analyses provides important and unique clues into the dynamics of fluid circulation and the influence of fluid–rock interaction on the carbon cycle within the forearc mantle in the hadal zone.

Results

Geological setting of the Izu–Ogasawara Trench and sampling. Samples of serpentinized peridotite were collected from the Umigame seamount (26°47'N, 143°14'E) on the forearc slope of the southern IOT (Fig. 1a, b). The IOT is an erosive trench^{36,37}, where deformation of the hangingwall occurs. Previous studies of the distribution of mafic and ultramafic rocks dredged from the IOT and geochemical and geochronological data have revealed that (i) outcrops of peridotite, gabbro, and dolerite occur from the slope base to slope top (7000–3000 mbsl) at the seamount³⁸, (ii) ultramafic rock is exposed on the slope at >5000 mbsl¹ (Fig. 1a), and (iii) the IOT comprises immature forearc mantle–crust related to subduction zone initiation^{38–40}.

During the YK17-14 Leg 2 cruise (July 2017) on the R/V *Yokosuka*, dive #1507 by the deep submergence research vehicle (DSV) *Shinkai 6500* collected 18 rock samples (14 serpentinized peridotites, 3 gabbros, and 1 basalt) from 6465 to 6429 mbsl at a water temperature of 1.7 °C, a salinity of 34.7 psu, and a dissolved oxygen content of 3.3 mL L^{−1} (6474 mbsl; Fig. 1c). The outcrop surveyed during dive #1507 consists of boulders of serpentinized peridotite (dominantly 10–50 cm in diameter, but up to 1–3 m) immersed in a muddy seafloor (Supplementary Fig. 1a, b). Boulder surfaces are mostly coated by black Mn deposits, although some have only thin coatings (Supplementary Fig. 1a, b). The serpentinite samples were originally mantled rocks (dunite and harzburgite). The samples are strongly serpentinized (~80%) and contain extensive fractures infilled with carbonate (Fig. 2a, b). X-ray diffraction and Raman spectra of the carbonate mineral indicate that it is pure aragonite. The aragonite is not observed on the surface of serpentinized peridotite but is limited to fractures (Fig. 2a). Unlike the serpentinite, carbonate veins have not been observed in the basalt and gabbros at the same location.

Petrology of aragonite-bearing serpentinized peridotite at depths of >6400 mbsl. One serpentinized harzburgite sample (6K#1507-R14) is highly brecciated, meaning that it is difficult to reconstruct its original structure (Fig. 2c; Supplementary Fig. 2a, b). Aragonite contains clasts of serpentine, olivine, and dendritic or spherical Mn oxides (Fig. 2c). High-resolution X-ray computed tomography imaging revealed that each clast is separated from other clasts and supported by aragonite (Fig. 2d). The clasts have a mode at ~100 µm diameter, but some measure up to 3–5 mm (Supplementary Fig. 2c). The serpentinite samples consist mainly of serpentine minerals (lizardite and chrysotile; $X_{\text{Mg}} = 0.91$; Fig. 2e, f) that are locally intermixed with talc. Magnetite and hematite, as well as variable amounts of aragonite, are also observed with relics of primary olivine ($X_{\text{Mg}} = 0.90$) and spinel (Fig. 2c). The serpentine has a mesh texture consisting of brown serpentine cores and white serpentine rims (Fig. 2e). Locally, voids up to ~100 µm in size are observed in the mesh cores (Fig. 2e, f), and some of the void inner walls are lined with hematite (Supplementary Fig. 3a, b). Back-scattered electron images of the serpentine mesh texture show that the brown serpentine cores have variable porosity (Fig. 2f). High-resolution focused ion beam–scanning electron microscopy (FIB–SEM) observations revealed the presence of abundant nano- to submicron-scale pores in the serpentine mesh cores, whereas nano-scale pores are less prominent in the serpentine mesh rims (Fig. 2g). Both the serpentine mesh cores and rims are cut by aragonite veins.

In the veins, aragonite shows radial growth features (Fig. 3a). In some samples (6K#1507-R12 and 6K#1507-R14; Supplementary Table 1), aragonite has grown in fractures and is acicular (1–5 mm in length; Fig. 2b), and the crystal surfaces of aragonite growing on fracture surfaces indicate crystal growth in some

Fig. 1 Location of the Shinkai dive #1507. **a** Bathymetric map of Izu-Ogasawara trench, with inset map showing the location of Japan and of the study area (red rectangle). The sampling location of serpentinized peridotite (6K#1507) is shown by a pink star, along with previous locations where peridotite or gabbro were recovered. **b** Enlarged bathymetric map of the area depicted by the black-and-white rectangle in Fig. 1a, around the Umigame seamount located in the southern Izu-Ogasawara Trench. Maps in **a** and **b** were drawn using Generic Mapping Tools 5.4.5⁹² with ETOPO1_Bed_g_gmt4.grd^{93, 94} (**a**) and grid data from the KR08-07 and KH07-02 cruises (**b**). **c** Depth profiles of seawater temperature, salinity, and dissolved oxygen (D.O.) during the DSV Shinkai 6500 dive #1507 (13 July 2017). The dive and sampling were conducted at ~6400 mbsl, which is deeper than both the carbonate (calcite) compensation depth (CCD; 4000–4500 mbsl)²⁷ and aragonite compensation depth (ACD; 500–1500 mbsl)³².

Fig. 2 In situ aragonite crystals from 6429 m below sea level from the YK17-14 Leg 2 cruise (6K#1507-R14). **a** Slice of serpentinite consisting of highly brecciated serpentine that is cemented by aragonite. **b** Euhedral aragonite in serpentinite fractures, which implies in situ aragonite growth. **c** Mineral-phase map created from an elemental map using k-means clustering. Ol = olivine; Srp = serpentine; Spl = spinel; Arg = aragonite. **d** Three-dimensional distribution of clasts (serpentine and olivine) in an aragonite vein (total volume: 1.13 mm × 0.90 mm × 0.89 mm). Photomicrograph (**e**) and back-scattered electron image (**f**) of serpentinite mesh texture, which consists of porous brown serpentinite mesh cores (b-Srp) and non-porous white serpentinite mesh rims (w-Srp). **g** FIB-SEM image showing the porosity contrast between the serpentinite mesh core and rim.

Fig. 3 Mineralogical and geochemical characteristics of the studied aragonite. **a** Radiating aragonite that infills between brecciated serpentinite clasts. SEM image of aragonite surface showing growth banding (**b**) and dissolution etch pits (**c**) in a single aragonite crystal. **d** Selected REE + Y (REY) patterns of the aragonite samples. **e** A comparison of C and O isotope data of this study with those of serpentine-hosted carbonate collected during previous dredges and dives. Data for aragonite-bearing serpentinitized peridotite recovered from hydrothermal fields are from Eickman et al.³¹ (Logachev and Gakkei ridges; 2000–4000 mbsl) and Ribeiro et al.²⁸ (Rainbow and Saldanha fields; 2200 mbsl). Aragonite in serpentinitized peridotite from the IOT is characterized by negative $\delta^{13}\text{C}$ values. Negative $\delta^{13}\text{C}$ values have been reported from the Mariana Trough²⁴, where cold and methane-rich seeps are observed. The red line and pink region indicate the $\delta^{18}\text{O}_{\text{V-SMOW}}$ value and $\pm 1\sigma$ range ($34.5\text{‰} \pm 0.7\text{‰}$) that is in equilibrium with seawater ($\delta^{18}\text{O}_{\text{V-SMOW}} = 0\text{‰}$) at 1.7°C . **f** Relationship between $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ of aragonite. The modern deep seawater $\Delta^{14}\text{C}$ value of DIC (-200‰ to -210‰)⁴² is represented by the green star. The inserted graph is a close-up view of the data. The analytical errors in **e** and **f** are substantially smaller than the symbols (Supplementary Table 1).

domains and dissolution (e.g., etch pits) in other domains (Fig. 3b, c).

Aragonite geochemistry. Geochemical analysis of aragonite veins from six bulk rock samples was conducted. The geochemistry of acicular aragonite observed in 6K#1507-R12 and 6K#1507-R14 was measured separately. The aragonite shows rare earth element (REE) and Y (REY) patterns (Fig. 3d) that are characterized by negative Ce anomalies ($\text{Ce}/\text{Ce}^* = 0.10\text{--}0.55$), depletion in LREEs relative to HREEs ($\text{Pr}_{\text{SN}}/\text{Yb}_{\text{SN}} = 0.57 \pm 0.41$), and high Y/Ho ratios ($42.6\text{--}73.2$; Supplementary Table 2). There are wide variations in the concentrations of aragonite ΣREY ($0.039\text{--}0.723 \mu\text{g g}^{-1}$) and U ($0.267\text{--}1.690 \mu\text{g g}^{-1}$; Supplementary Table 2). The acicular aragonite has a higher ΣREY relative to aragonite veins from the same rock sample (Supplementary Table 2). The Sr/Ca ratio of the fluid reconstructed from the aragonite composition ($\text{Sr}/\text{Ca} = 11.4\text{--}15.5 \text{ mmol/mol}$; Supplementary Table 2) is $9.68\text{--}13.13 \text{ mmol/mol}$, which is high compared with modern seawater ($\text{Sr}/\text{Ca} = 8.7 \text{ mmol/mol}$)⁹.

Aragonite $\delta^{13}\text{C}_{\text{V-PDB}}$ values vary from -2.0‰ to $+0.1\text{‰}$ (Fig. 3e; Supplementary Table 1). $\delta^{18}\text{O}_{\text{V-SMOW}}$ values of the aragonite ($33.80\text{‰} \pm 0.01\text{‰}$ to $36.19\text{‰} \pm 0.01\text{‰}$; Supplementary Table 1) are mostly in the range of aragonite $\delta^{18}\text{O}_{\text{V-SMOW}}$ values in equilibrium with seawater at 1.7°C ($34.5\text{‰} \pm 0.7\text{‰}$; Fig. 3e), although some aragonite samples are slightly enriched in ^{18}O (Fig. 3e). $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of most aragonite samples ($0.70915\text{--}0.70916$; Supplementary Table 1) are similar to that of

modern seawater (0.70917)⁴¹, with some having slightly higher (6K#1507-R14: 0.709195) or lower (6K#1507-R01: 0.709099) values (Supplementary Table 1).

The radiocarbon ($\Delta^{14}\text{C}$) contents of the aragonite samples analyzed in this study range from -991‰ to -995‰ (Fig. 3f; Supplementary Table 1). All $\Delta^{14}\text{C}$ values of the studied aragonite are quite different from that of present-day seawater at a similar depth in the IOT ($\Delta^{14}\text{C} = -200\text{‰}$ to -210‰ ; Fig. 3f). Vein-filling and acicular aragonite sampled from the same rock specimen (6K#1507-R14) have similar $\Delta^{14}\text{C}$ values, -994‰ and -995‰ , respectively (Supplementary Table 1). The process blank obtained from the ^{14}C -free standard IAEA-C1 yielded 0.0037 ± 0.0001 Fraction Modern ($\Delta^{14}\text{C} = -996.3\text{‰}$), indicating that the aragonite samples are nearly ^{14}C dead (Supplementary Table 1).

Discussion

Serpentinized peridotites are commonly found along the trench-landward slope of the western Pacific margin, as well as in the IOT and Mariana trench^{1,43}. The studied samples from the Umigame seamount were obtained from $\sim 6400 \text{ m}$ water depth, indicating that our observations in this study are consistent with those of previously investigated occurrences of ultramafic rock^{1,38,44} (Fig. 1a). Moreover, peridotite occurrence is limited to water depths of $>5000 \text{ m}$ in the IOT (Fig. 1b) and no serpentinitized peridotite has been reported above the ASD ($500\text{--}1500 \text{ mbsl}$)^{1,38,40}, where aragonite can precipitate directly from

seawater, suggesting that the recovered rocks did not originate from the shallow ocean floor. Therefore, aragonite-bearing serpentinized peridotite was formed by autochthonous processes in the hadal seafloor.

Textural relationships and the presence of olivine in aragonite veins (Fig. 2c) suggest that serpentinization was incomplete due to its sluggish kinetics, and aragonite precipitation postdated the serpentinization. The radial texture of the aragonite (Fig. 3a) indicates that it was precipitated under supersaturated conditions, although hadal seawater is undersaturated in aragonite (Fig. 1c). Both the presence of fractures and the composition of the bulk rock are inferred to play a key role in aragonite formation, as no carbonate was observed in fractures in both gabbro and basalt samples recovered adjacent to aragonite sampling points (Supplementary Fig. 4a, b), and, in particular, aragonite is not observed on rock surfaces either (Fig. 2a).

Furthermore, $\delta^{13}\text{C}_{\text{V-PDB}}$ values (-2.0‰ to $+0.1\text{‰}$; Fig. 3e) of the studied aragonite are similar to those of dissolved inorganic carbon (DIC) in seawater ($\delta^{13}\text{C}_{\text{V-PDB}} = 0\text{‰}$), suggesting that the aragonite was formed from DIC derived from seawater. The similarity of aragonite $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to that of modern seawater also supports a seawater origin. In addition, the REY pattern of the aragonite samples is characterized by negative Ce anomalies, positive Y anomalies, and elevated Y/Ho mass ratios (Fig. 3d), suggesting that the fluid source for the aragonite was predominantly seawater. The depletion in LREEs and variation in ΣREY imply a change in fluid source and the influence of sedimentary porewater^{45,46}.

Hadal zone is undersaturated to precipitate aragonite directly from seawater (Fig. 1c). Calculations based on oxygen isotopic fractionation at ambient seawater temperatures (1.7°C) indicate that the aragonite was precipitated from seawater with $\delta^{18}\text{O}_{\text{V-SMOW}} = 1.6\text{‰} \pm 0.6\text{‰}$, which differs from ambient seawater ($\delta^{18}\text{O}_{\text{V-SMOW}} = 0\text{‰}$) but is consistent with the $\delta^{18}\text{O}_{\text{V-SMOW}}$ values of serpentinizing fluids from different locations^{2,23,44}. Thus, the geochemical evidence reveals that the chemical composition of seawater that induced aragonite formation was slightly different from that of ambient seawater.

There are two possible causes of the presence of ^{14}C -dead carbon in the aragonite: (i) the aragonite was formed from ^{14}C -bearing seawater and survived dissolution for some time; or (ii) the aragonite was formed more recently from almost- ^{14}C -dead seawater. During dive observations, we did not observe active venting of fluids, meaning that aragonite-supersaturated fluid is not presently forming on serpentinized peridotite. This finding implies that preexisting aragonite is being dissolved in the hadal ocean. The surface morphology of aragonite suggests that dissolution is ongoing (Fig. 3c), but aragonite dissolution in the hadal ocean (i.e., below the ACD) would be completed rapidly, as revealed by in situ carbonate dissolution experiments⁴⁷. Therefore, the former scenario is unlikely, and the preservation of aragonite on the hadal seafloor suggests recent aragonite formation, which is inconsistent with the obtained ^{14}C results. The ^{14}C of aragonite hence represents not the age of aragonite formation but a carbon source composed of ^{14}C -dead carbon; the deviation of $\Delta^{14}\text{C}$ content between aragonite and modern deep seawater (Fig. 3f) suggests that aragonite formation was sourced from nearly ^{14}C -dead carbon in seawater that had stagnated in the serpentinized peridotite. The blank-corrected ^{14}C ages of sample 6K#1507-R13 and modern hadal water in the IOT ($\Delta^{14}\text{C} = -206.6\text{‰} \pm 4.4\text{‰}$)⁴² are $44,230 \pm 600$ and 1860 ± 50 BP, respectively, implying that the residence time of fluids in the serpentinized peridotites is >42 kyr.

Thermodynamic calculations of seawater–mantle rock equilibrium (i.e., with serpentinite) at 1.7°C and 65 MPa reveal that brucite concentrations decrease with increasing seawater reaction

(i.e., increasing the fluid-to-rock mass ratio, F/R ; Supplementary Fig. 5). Therefore, the lack of brucite in the serpentinized peridotite from the IOT suggests that brucite was consumed during seawater–serpentinite reactions^{29,48}. Moreover, the modeling revealed that the observed aragonite-bearing mineral assemblage (talc + serpentine + hematite + aragonite) is stable at a high F/R ($= 10^{2.5}\text{--}10^{3.5}$; Supplementary Fig. 5). The high F/R ratio for aragonite precipitation is consistent with seawater-like REY patterns and C–O–Sr isotope data, as this ratio implies only a small change in the composition of seawater by reactions with mantle rock. These calculations suggest that aragonite formation occurs as a consequence of seawater–serpentinite reaction under the conditions of the hadal ocean and in the presence of a high paleoseawater flux.

The occurrence of rock fragments supported within aragonite veins indicates that the flow of fluid (paleoseawater) balanced the ambient seawater pressure. The Ergun equation⁴⁹, which has been used to estimate fluid velocity^{50–54}, was also applied to the supported clasts in the aragonite veins (Fig. 2b). Image analysis constrained the extent of serpentinization and degree of porosity in the serpentinite clasts to 80%–100% and 0%–50%, respectively (Fig. 2c). Using these values, we obtained a fluid flow velocity of $10^{-2}\text{--}10^{-1} \text{ m s}^{-1}$ for 3–5-mm-diameter clasts to be suspended in the fluid (Supplementary Fig. 6). The discharge velocity is consistent with those measured in hydrothermal vents ($0.02\text{--}1.99 \text{ m s}^{-1}$)⁵⁵. Moreover, we estimated the duration of the fluid (paleoseawater) discharge involved in the precipitation of aragonite using the estimated fluid velocity. Given a fracture length scale of 100 m, we obtained a timescale for fluid flow of 10–10,000 days. The estimated timescale for fluid flow and carbonate precipitation is largely consistent with the observation that a carbonate–brucite chimney can be produced in a year⁵⁶ at a serpentinized fluid seep. These results suggest that rapid venting of paleoseawater from forearc serpentinite can be surprisingly short-lived and pulse-like.

The samples of serpentinized peridotite investigated in this study were recovered from the inner-wall trench, which is ~ 10 km landward of the IOT (Fig. 1a, b). At the forearc front, fluids released by compaction from subducting sediment generally have a chemical composition that is similar to that of seawater⁵⁷. In accreting margins, fluid flow is largely constrained by matrix permeability, and fluid thus migrates along the décollement or as diffuse flow across the accreted overriding sediments⁵⁸. In contrast, in an erosive margin such as the IOT, fluid flow across the overriding rock is controlled by faults because the bulk of the upper plate of an erosive margin has low permeability⁵⁹. Fluids thus accumulate in and migrate through fractures in the overriding plate to the ocean^{60,61}. The fracture can be created by various processes. Fluid overpressure commonly observed at the plate interface^{57,61–63} induces hydrofracturing of the base of the overriding rock in the erosive margin, which allows the migration of fluids into the overriding rock^{59,61,64}. Moreover, present-day tectonic stresses related to tectonic erosion would induce pervasive normal faulting^{64,65}. Either or both of these processes may create interconnected fractures across the overriding serpentinized peridotite at the erosive margin, resulting in discharge of the stagnated fluid from serpentinized peridotite to hadal seafloor. Considering that the growth rates of hydrogenetic crust ($1\text{--}10 \text{ mm Myr}^{-1}$)^{66,67} are similar in a wide range of water depths ($800\text{--}5500 \text{ mbsl}$)⁶⁸, thin ($<1 \text{ mm}$ thick) Mn coatings on the surfaces of the samples recovered from $\sim 6400 \text{ mbsl}$ (Supplementary Fig. 1a, b) indicate that deformation of the rocks occurred prior to $1.0\text{--}0.1 \text{ Ma}$.

Given the above discussion, we propose the following model of fluid flow dynamics in tectonically exposed forearc mantle: (i) Seawater trapped in subducting sediments are expelled by compaction just after subduction and accumulate in the overriding

Fig. 4 Fluid dynamics in the tectonically exposed forearc mantle. **a** Schematic illustration of the erosive convergent margin in the IOT and DSV *Shinkai* 6500. **b** Simplified illustration of the area represented by the dashed gray rectangle in **a**, showing fluid circulation in the tectonically exposed forearc mantle. **c** Fluid flow and carbonation at fracture indicated by the dashed gray rectangle in **b**. Schematic illustration of the episodic rupture events that allow the accumulated seawater to discharge. Each event continues for 10^1 to 10^4 days with a velocity of 10^{-2} to 10^{-1} m s $^{-1}$ and induces carbonation.

tectonically exposed forearc serpentinitized peridotite (Fig. 4a, b); (ii) the seawater with dissolved carbon stagnates for >42 kyr within the serpentinitized peridotite (Fig. 4b); and (iii) episodic rupture events expel these deep-seated carbon-bearing fluids and lead to aragonite precipitation (Fig. 4c). Subsequent exposure to hadal seawater leads to rapid carbonate dissolution⁴⁷, meaning that these processes recycle the accumulated carbon to the ocean (Fig. 4b, c). Recent studies have revealed that subducted carbon is sequestered in the forearc crust and mantle, thereby influencing the global carbon cycle^{18,21,22,69–71}. The residence time of carbon in the forearc is related to the reservoir size and determines the response of carbon flux into the atmosphere and biosphere induced by the perturbation of carbon flux¹⁷. Our estimate of the residence time of circulating carbon-bearing fluids in serpentinitized peridotite (ca. > 42 kyr) is much longer than that for thermally driven hydrothermal fluid flow along fractures in the oceanic crust at mid-ocean ridge settings (less than a few years)^{34,72}. The lower bound of residence time obtained in this study is similar to the carbon residence time in the forearc (88–8800 kyr)^{18,73}, implying that the exposed forearc mantle may also be a large reservoir of carbon and water and may reduce carbon flux to deep regions of Earth (Fig. 4b). Compared with the residence time of carbon in the global carbon cycle in subduction zones (in the order of 10 Myr)^{17,19}, the lower bound of residence time is much shorter, suggesting that the exposed forearc serpentinitized peridotite can act as a shortened pathway for the carbon cycle and respond quickly to ongoing perturbation in subducting carbon input fluxes¹⁷. We infer that aragonite deposition on exposed forearc mantle peridotite may induce episodic carbon flux perturbation, causing an imbalance in the geological carbon cycle, ultimately influencing the atmosphere, climate, ocean, and habitability of Earth.

Methods

Submersible conductivity–temperature–depth profiler. The depth profiles of seawater temperature, salinity, and dissolved oxygen were obtained with a submersible conductivity–temperature–depth (CTD) profiler system (SBE-19 SEA-CAT PROFILER CTD and SBE43 DO; Sea-Bird Electronics Inc.) mounted on the submersible research vehicle *Shinkai 6500*⁷⁴. Conductivity, water temperature, pressure, and dissolved oxygen were measured in 1 time in a second.

Scanning electron microscopy (SEM). SEM was undertaken at the JAMSTEC on Au-coated samples with an FEI Quanta instrument operated at an accelerating voltage of 15–30 kV.

Electron probe microanalysis (EPMA). Chemical compositions of minerals were analyzed by EPMA (JEOL JXA8500F) at the JAMSTEC. The accelerating voltage and electron beam current were 15 kV and 1–12 nA for point analysis, and 15 kV

and 50 nA for elemental mapping, respectively. ZAF corrections were applied to the raw data.

Image analysis. The clast size distribution of the serpentinite was obtained from an EPMA elemental map using ImageJ software. A Ca elemental map (2 cm × 2 cm) with a pixel size of 10 μm was used to obtain the clast size distribution. The clast diameter was calculated based on the equivalent diameter. Owing to the spatial resolution of the images used for the analysis, a cut-off value of 25 square pixels was defined.

X-ray diffraction (XRD). X-ray powder diffraction analysis was performed by XRD (Rigaku RINT-220VL), using Cu-Kα radiation. Samples were scanned with 2θ step sizes of 0.02°.

Raman microscopy. Raman microscopy was conducted with a Raman spectrophotometer (Nanophoton RAMANtouch) at the JAMSTEC using a 532 nm green laser. The laser power was 2–10 mW on the sample surface. Most spectra were collected using a 1200 grooves mm $^{-1}$ grating. The Raman peak position was calibrated using a silicon wafer (520.7 cm $^{-1}$).

X-ray computed tomography (X-ray CT). A quadrangular prism (5 mm wide) was cut from the serpentinitized peridotite and scanned using high-resolution X-ray computed tomography (Xradia 410 Versa ZEISS) at the Kochi Core Center, Kochi, Japan. Images were obtained under conditions of 70 kV beam energy, 8 W power, and 10 s exposure time using 360° rotation. We collected 3201 projections. The images had a pixel size of 3.0 μm and were visualized using the software program Fiji⁷⁵.

Focused ion beam–SEM (FIB–SEM). Cross-sectional microtextures were investigated using a dual-beam FIB–SEM system (Helios G4 UX; Thermo Fisher Scientific) at the JAMSTEC. A gallium ion source installed at an angle of 52° was used to mill the sample. After careful determination of the target area, a 1-μm-thick platinum layer was deposited on the area of interest to protect it from ion beam damage. FIB serial sectioning was performed using an ion beam of 30 kV and 9.1 nA. Images taken using the mirror detectors were processed with Adobe Photoshop® software to adjust the contrast and brightness.

Trace-element analyses. Aragonite sample powders weighing between 20 and 50 mg were placed into vials containing 0.5 mL of distilled water and 0.2 mL of CH₃COOH. After dissolution and drying, a mixed acid solution (nitric, hydrochloric, and hydrofluoric acids) was used to dissolve the powders, which were then dried three times. The solution was diluted by a factor of 10,000 for REE measurements and by a factor of 50,000 for Mn measurements. All analyses were carried out using an ICP–MS instrument at Niigata University, Japan, using the procedures of Neo et al.⁷⁶. The BHVO-2, W-2a, and JB-2 standards were also analyzed. Eu, La, Gd, and Ce anomalies were calculated using shale-normalized (SN) concentrations as follows: $\text{Eu}/\text{Eu}^* = 2\text{Eu}_{\text{SN}}/(\text{Sm}_{\text{SN}} + \text{Gd}_{\text{SN}})$ ⁷⁷, $\text{La}/\text{La}^* = \text{La}_{\text{SN}}/(\text{Pr}_{\text{SN}}(\text{Pr}_{\text{SN}}/\text{Nd}_{\text{SN}})^2)^{78}$, $\text{Gd}/\text{Gd}^* = \text{Gd}_{\text{SN}}/(\text{Tb}_{\text{SN}}(\text{Tb}_{\text{SN}}/\text{Dy}_{\text{SN}}))^{79}$, and $\text{Ce}/\text{Ce}^* = \text{Ce}_{\text{SN}}/(\text{Pr}_{\text{SN}}^2/\text{Nd}_{\text{SN}})^{77}$. Trace-element compositions and anomalies are presented in Supplementary Table 2. The Post-Archean Australian Shale values used for normalization were taken from McLennan⁷⁹.

Calculation of fluid Sr/Ca ratios. The fluid Sr/Ca molar ratio ($[\text{Sr}/\text{Ca}]_{\text{fluid}}$) was determined from:

$$\frac{[\text{Sr}]}{[\text{Ca}]}_{\text{fluid}} = \frac{[\text{Sr}/\text{Ca}]_{\text{Aragonite}}}{K^{\text{Sr}-\text{Ca}}}, \quad (1)$$

where $[\text{Sr}/\text{Ca}]_{\text{Aragonite}}$ is the Sr/Ca molar ratio of aragonite, and $K^{\text{Sr}-\text{Ca}}$ is the equilibrium partition coefficient for Sr between aragonite and fluid. The temperature (T ; in K) dependent partition coefficients are given by:⁸⁰

$$K^{\text{Sr}-\text{Ca}} = 1.2488 - 0.0044(T - 273). \quad (2)$$

Carbon and oxygen isotope analyses. Aragonite powder samples were placed in small stainless steel thimbles and dropped into a reaction vessel containing pyrophosphoric acid at 60 °C in a vacuum to liberate CO_2 gas. The CO_2 was cleaned cryogenically to remove impurities such as H_2O with pentane slush and collected using a liquid nitrogen cold trap. Stable-isotope measurements were carried out with a Thermo Fisher MAT-253 mass spectrometer at Niigata University. The results are reported in conventional δ notation in per mil (‰) with respect to Vienna Standard Mean Ocean Water (V-SMOW) for oxygen isotopes and Vienna Pee Dee Belemnite (V-PDB) for carbon isotopes. The precisions of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for the laboratory standard CO_2 gas were $\pm 0.03\text{‰}$ and $\pm 0.05\text{‰}$, and for NBS-20 were $\pm 0.05\text{‰}$ and $\pm 0.1\text{‰}$, respectively. Stable-isotope results are presented in Supplementary Table 1.

$\delta^{18}\text{O}$ fractionation between aragonite and fluid. We used the following equilibrium oxygen isotope fractionation equation between aragonite and fluid proposed by Kim et al.:⁸¹

$$1000\ln\alpha = 17.88 \pm 0.13 \left(\frac{10^3}{T} \right) - 31.14 \pm 0.46 \quad (3)$$

where α is the fractionation factor between aragonite and water, and T is the temperature in K. $\delta^{18}\text{O}$ values of aragonite in equilibrium with seawater (Fig. 3e) were calculated using the above equation, as well as a seawater temperature of 1.7 °C and seawater $\delta^{18}\text{O} = 0\text{‰}$. $\delta^{18}\text{O}$ values of the fluids were calculated using the above equation, a seawater temperature of 1.7 °C, and the measured aragonite $\delta^{18}\text{O}$ values (Supplementally Table 1).

Strontium isotopes. Strontium isotopes were measured on an aliquot of the same sample powders used for the analysis of stable isotopes and trace elements. Aragonite samples were firstly decomposed in a mixed solution of distilled water and CH_3COOH in a Teflon® vessel. Only carbonate minerals dissolve in acetic acid, which minimizes the effect of any minor silicate minerals, especially detrital components, on the strontium isotopic composition. After dissolution, the vials were centrifuged, and the supernatant was separated. Distilled water was added once again to the residue, and the supernatant was collected. The collected supernatant liquid was evaporated to dryness and nitric acid was added to the residue. Ca–Rb–Sr and REEs were separated in a first column separation (BioRad, AG50W-X8 cation exchange resin). Purification of strontium was undertaken with a second column separation (Eichrom Sr-Spec resin). Rubidium–Sr isotope analyses were carried out following the procedures of Miyazaki and Shuto⁸² by thermal ionization mass spectrometry with a Finnigan MAT 262 mass spectrometer at Niigata University. A tantalum (sample) and rhenium (ionization) filament combination was used for the analysis. Strontium isotopic compositions were normalized to $^{87}\text{Sr}/^{86}\text{Sr} = 0.1194$. Repeated measurements of the strontium isotopic composition of the NIST 987 standard agree well with the known values for this standard ($^{87}\text{Sr}/^{86}\text{Sr} = 0.710251 \pm 0.000003$; 2σ ; $n = 20$). The 2σ values of the carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were less than ± 0.000014 (Supplementally Table 1).

Radiocarbon analysis. Hand-picked aragonite was rinsed with 0.1 M HCl acid for a few minutes. Approximately 10–15 mg of aragonite sample powders and 5 mL of phosphoric acid were introduced into a bifurcated reactor and connected to the vacuum line. After being a vacuum and sealed, the sample was reacted with phosphoric acid at 60 °C overnight to produce CO_2 gas. The CO_2 gas of about 1–3 mgC was cryogenically purified in a vacuum line using liquid N_2 , ethanol/liquid N_2 , and n-pentane traps. The purified CO_2 of ~1 mgC was reduced to graphite by H_2 with a Fe catalyst at 620 °C for 6 h. The resulting mixture of graphite and Fe powder was pressed into a target holder for AMS ^{14}C measurements. The ^{14}C concentrations were measured with a Tandem AMS (model 4130-AMS, HVEE) at the Institute for Space-Earth Environmental Research, Nagoya University, Japan, by comparison to NIST oxalic acid (SRM 4990C: OxII). Each target was ^{14}C -measured for five runs of 30 min each with the AMS. The $^{12}\text{C}^{3+}$ beam currents were 100–200 nA during the measurement runs. The isotopic fractionation was corrected using the $^{13}\text{C}/^{12}\text{C}$ ratio measured by the AMS systems. ^{14}C contents are reported as $\Delta^{14}\text{C}$ (Supplementally Table 1).

Geochemical modeling. Geochemical modeling was conducted with Geochemist's Workbench 12® software (GWB)⁸³. The isobaric (65 MPa) thermodynamic dataset was generated based on a SUPCRT92⁸⁴ speq06.dat dataset using DBCreate

software⁸⁵. The saturation state of minerals and redox potential of seawater at 1.7 °C and 65 MPa were calculated with the SpecE8 module in GWB. The seawater composition used was the bottom seawater composition of the Mariana Trench (Supplementary Table 3)⁴¹, with modifications to the Fe and $\text{O}_{2(\text{aq})}$ concentrations. The Fe concentration was set to $1.0 \times 10^{-6} \text{ mol kg}^{-1}$ on the basis of the detection limit of the ICP-OES analyses, and the $\text{O}_{2(\text{aq})}$ content (3.3 mL L^{-1}) is the measured value in the IOT (Fig. 1c). Reaction path modeling was conducted with the REACT module in GWB by suppressing calcite, dolomite, and magnesite from the thermodynamic dataset. It is known that these suppressed minerals are difficult to be precipitated from seawater at ambient temperatures, even under supersaturated conditions. Suppression of the mineral phases was undertaken at the discretion of the operator, based on the feasibility of such minerals being precipitated, as recommended by the modeling package⁸³. In the reaction path modeling, serpentine is titrated step by step in 1 kg of seawater, with a composition identical to that used for calculation of mineral saturation (Supplementary Table 3). Modeling results are monitored by the fluid-rock mass ratio (F/R). In terms of the modeling on fluid infiltration into fractures, large F/R show equilibrium mineral assemblage of fluid-dominated conditions (e.g., around fracture) whereas low F/R show that of rock-dominated conditions (e.g., far from the fracture)^{29,70,86–88}. The serpentine was assumed to consist of chrysotile (85 mol%), brucite (10 mol%), and magnetite (5 mol%). We did not consider mineral solid solutions, and thus our simulation is a simplified approach.

Estimation of fluid velocities and timescales. The Ergun equation provides an estimate of fluid velocities (v ; m s^{-1}) for fluidization and elutriation:^{49–51}

$$\frac{\Delta p}{H} = \frac{150\mu(1-\varepsilon)^2 v}{\Psi^2 \varepsilon^3 d_p^2} + \frac{1.75(1-\varepsilon)\rho v^2}{\Psi \varepsilon^3 d_p} \quad (4)$$

where Δp (Pa) is the reduction in fluid pressure; H (m) is the height of the fluidized layer; Ψ is the particle sphericity; μ (Pa s) and ρ (kg m^{-3}) are the fluid viscosity and density, respectively; and d_p (m) is the particle diameter; ε is the proportion of voids relative to particles + fluid. When the force exerted on particles by the upward fluid flow equals the gravity force on the particles, the $\Delta p/H$ ratio is given by:

$$\frac{\Delta p}{H} = (\rho_p - \rho)(1 - \varepsilon)g, \quad (5)$$

where ρ_p (kg m^{-3}) and g (m s^{-2}) are the particle density and acceleration due to gravity, respectively. These two equations can be combined and solved to estimate the minimum fluidization velocity (v_m):

$$v_m = \frac{150\mu(\varepsilon - 1) + \sqrt{(150\mu(1 - \varepsilon))^2 + 7g\rho(\rho_p - \rho)\varepsilon^3 d_p^3}}{3.5\rho d} \quad (6)$$

For packed aggregates, Wen and Yu⁸⁹ proposed that the void proportion at the minimum fluidization velocity (ε_{mf}) is empirically related to the particle sphericity as $\varepsilon_{mf} = (0.071/\Psi)^{(1/3)}$. The velocity required to elutriate a spherical particle (v_t) is given by:

$$v_t = \sqrt{\frac{3(\rho_p - \rho)gd_p}{\rho}} \quad (7)$$

In our calculations, μ and ρ were set to 1.17×10^{-3} (Pa s) and 1028 (kg m^{-3}), respectively, based on the properties of seawater at 2 °C.

The serpentine clasts exhibit variable degrees of serpentinization and reaction-induced porosity (Fig. 2c). These effects on density can be expressed as:

$$\rho_p = \rho_{\text{Srp}}(1 - \varphi_p) \quad (8)$$

where φ_p is the porosity of a serpentine clast; and ρ_{Srp} (kg m^{-3}) is the density of serpentinized peridotite, which is obtained from the empirical relationship between the extent of serpentinization and density proposed by Miller and Christensen:⁹⁰

$$\rho_{\text{Srp}} = 1000 \left(3.3 - 0.785 \frac{\xi_{\text{Srp}}}{100} \right) \quad (9)$$

where ξ_{Srp} (%) is the degree of serpentinization.

Supplementary Fig. 7 shows the relationship between porosity and serpentinization and density calculated from Eqs. (8–9), which suggests that φ_p has a large effect on the calculated density compared with ξ_{Srp} . Preservation of clasts in the breccia indicates that the clast density is greater than the seawater density. Therefore, the seawater density contour can be used to constrain the upper limit of φ_p . Mineralogical observations suggest that ξ_{Srp} ranges from 80% to 100% and that the two-dimensional porosity varies from 0% to 50% (Fig. 2c, d). From these ranges, two end-member cases for the extent of serpentinization (ξ_{Srp} ; %) and porosity (φ_p) in the serpentine clasts were examined: $\xi_{\text{Srp}} = 80\%$ and $\varphi_p = 0$ ($\rho_p = 2672 \text{ kg m}^{-3}$) as an upper limit for ρ_p ; and $\xi_{\text{Srp}} = 100\%$ and $\varphi_p = 0.5$ ($\rho_p = 1257 \text{ kg m}^{-3}$) as a lower limit for ρ_p .

The estimated velocity can be used to estimate the timescale of fluid flow. The time-integrated volumetric fluid flux (Q ; $\text{m}^3 \text{fluid m}^{-2} \text{rock}$) is given by:

$$Q = \int_0^t v \phi dt, \quad (10)$$

where t (s) is the duration of water flow, and ϕ is the fracture porosity. Assuming local equilibrium between the fluid and rock, the time-integrated fluid flux is given by:⁹¹

$$Q \approx L \frac{M_e}{\Delta C_e} + L \phi, \quad (11)$$

where L (m) is the characteristic length, M_e ($\text{mol m}^{-3} \text{rock}$) is the moles of element e added or removed per volume of rock, and ΔC_e ($\text{mol m}^{-3} \text{fluid}$) is the concentration difference of element e between the input and equilibrium fluids. $M_e/\Delta C_e$ is equivalent to the fluid–rock volume ratio and can be rewritten as $M_e/\Delta C_e = (M_f/M_r)(\rho_r/\rho)$, where M_f (kg) is the mass of fluid reacted with the initial rock mass (M_r ; kg), ρ (1028 kg m^{-3}) is the seawater density at 2°C , and ρ_r (kg m^{-3}) is the density of the initial rock calculated from its empirical relationship with the extent of serpentinization (i.e., Eq. (9); $\rho_r = \rho_{\text{Srp}}$). M_f/M_r is the fluid–rock mass ratio and is equivalent to F/R in the reaction path simulation (i.e., $M_f/M_r = F/R$). The two equations for Q are combined and provide estimates of the timescales:

$$t = \frac{L}{v} \left(\frac{M_f \rho_r}{M_r \rho} \phi^{-1} + 1 \right). \quad (12)$$

From petrological observations, we assumed that the extent of serpentinization (ξ_{Srp}) is 30%–100%. The ξ_{Srp} range constrains the ρ_r range to 2515–3064 kg m^{-3} . A range of F/R of $10^{2.5}$ – $10^{3.5}$ was constrained by thermodynamic modeling (Supplementary Fig. 5), and a range of v of 10^{-2} – 10^{-1} was constrained by numerical modeling (Supplementary Fig. 6). The range of ϕ was assumed to be 0.1–0.8. Using these values and a fracture length of 100 m ($L = 100$), a minimum estimate of the timescale can be calculated as follows:

$$t = \frac{100}{10^{-1}} \left(10^{2.5} \frac{2515}{1028} 0.8^{-1} + 1 \right) = 9.6 \times 10^5, \quad (13)$$

which is equal to 10 days. Similarly, the maximum timescale can be calculated as follows:

$$t = \frac{100}{10^{-2}} \left(10^{3.5} \frac{3064}{1028} 0.1^{-1} + 1 \right) = 9.4 \times 10^8, \quad (14)$$

which is equal to 10,000 days. Thus, we constrained the timescale to be 10–10,000 days.

Data availability

The data of this study are available in Supplementary Tables and the online repository at: <https://doi.org/10.6084/m9.figshare.16816099>.

Code availability

The code used for thermodynamic modeling (The Geochemist's Workbench®) can be purchased from Aqueous Solutions LLC (<https://www.gwb.com/index.php>).

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Author contributions

R.O., A.O., Y.H., and K.M. joined the YK17-14 science party and collected samples. R.O., A.O., and K.M. designed the project. M.S.-K. conducted the C–O–Sr isotope and trace element analyses. R.O. and M.M. undertook the radiocarbon dating. R.O. made the petrological observations and conducted the geochemical and numerical modeling. All authors contributed to the data interpretation. R.O. prepared the draft of the manuscript. All authors were involved in revising the manuscript and approved the submitted version.

Competing interests

The authors declare no competing interests.

Additional information

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