Rupture of wet mantle wedge by self-promoting carbonation

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More than one teramole of carbon per year is subducted as carbonate or carbonaceous material. However, the influence of carbonation/decarbonation reactions on seismic activity within subduction zones is poorly understood. Here we present field and microstructural observations, including stable isotope analyses, of carbonate veins within the Higuchi serpentinite body, Japan. We find that the carbon and oxygen isotope compositions of carbonate veins indicate that carbonic fluids originated from organic materials in metasediments. Thermodynamic calculations reveal that carbonation of serpentinite was accompanied by a solid volume decrease, dehydration, and high magnesium mobility. We propose that carbonation of the mantle wedge occurs episodically in a self-promoting way and is controlled by a solid volume contraction and fluid overpressure. In our conceptual model, brittle fracturing and carbonate precipitation were followed by ductile flow of carbonates and hydrous minerals; this might explain the occurrence of episodic tremor and slip in the serpentinized mantle wedge.
ubduction zones transport surface materials deep into Earth’s interior. Metamorphism of subducted lithosphere releases water and CO₂ to the overlying accretionary prism or mantle wedge1-6. Subduction zone fluids contain various chemical species and have a wide range of pH that varies in response to P–T conditions7-9. Large gradients in temperature and chemical potential along the subduction interface generate ideal conditions for mineral dissolution, precipitation, and metasomatism10-12. Such chemical reactions can change mechanical strength, permeability, and fluid pressure, and thus influence the rheological and seismological characteristics of subduction zones13. For example, silica precipitation may control the recurrence periods of ordinary earthquakes13 and slow earthquakes within subduction zones14.

Along the slab–mantle interface below the forearc Moho, hydration of mantle peridotite forms serpentine minerals and hydrous metasomatic minerals such as talc, amphibole, phlogopite, and chlorite14,15-18. Hydration can lower fluid pressure, and the plastic flow or frictional sliding of hydrous minerals result in steady-state slip18. Therefore, the downdip limit of large earthquakes (seismogenic zone) can be defined either by the brittle–ductile transition in crustal rocks (i.e., 350–400 °C) or the intersection of the subduction thrust and the forearc Moho10,19.

Slow slip events (SSEs) are observed at depths corresponding to the transition between the seismogenic zone and the deeper stably sliding zone. Slow slip events include long-term slip events that occur in relatively shallow parts of the subduction interface, and episodic tremor and slip (ETS) in relatively deep parts. In warm subduction zones such as Nankai and northern Cascadia, ETS is abundant in the corner of the mantle wedge, a region that could be dominated by serpentine formed by fluids released from the subducting slab. Several geological models involving chemical reactions have been proposed to explain ETS, including those that involve silica precipitation14,24 and the formation of carbonaceous materials14,27. Because most metasomatic reactions that occur in serpentinitized mantle release liquid water10,12,27, mechanical instabilities might be generated by fluid overpressure. However, the build-up of fluid overpressure is controlled by various factors including the relative rates of fluid generation, pore generation, and pore collapse28,29, and the geological mechanisms controlling the interplay between these factors in the ETS source region remain debated.

Estimates of the carbon budget in subduction zones suggest that more than one teramole of carbon is subducted each year as carbonates or carbonaceous materials1,2,26. The nature of carbon-bearing fluids (e.g., carbon dioxide, methane) and their interaction with rocks are highly sensitive to redox conditions31. Graphite has been considered as a sink of carbon within the subducting slab due to its low solubility in fluids31. However, recent experimental and thermodynamic modeling studies have revealed that graphite solubility is enhanced by pH and dissolved silica32, and that the dissolution of carbonaceous materials in sediments plays an essential role in generating carbon-bearing fluids in subduction zones33. Carbon-bearing fluids are also produced by the decomposition of carbonates via infiltration of H₂O-rich fluids1,2,5 and by fluid-induced dissolution of carbonate minerals coupled with precipitation of silicate minerals11. In particular, mantle peridotite has the potential to influence deep carbon cycling by acting as a voluminous sink of CO₂. Carbonation of exhumed oceanic mantle and carbon storage within ophiolitic rocks are commonly reported34, whereas the behavior of carbon-bearing fluids in subduction-related serpentinites is more complex35-39. When carbonates are in contact with serpentinite, graphite is often formed due to the relatively reducing conditions associated with serpentinite35,36. In contrast, reports of high-pressure carbonated serpentinites related to subduction zones37-39 highlight the potential for long-term CO₂ sequestration in the subducting slab and mantle wedge, even although some studies suggest that most subducted carbonate is recycled back to the surface40. In addition, carbonation and decarbonation reactions can induce changes to the mechanical properties of mantle rocks. For example, infiltration of reducing fluids can promote strain localization in carbonated serpentinites, implying that carbonic fluids could have an influence on earthquake processes in subduction zones41. Experiments involving in situ carbonation of antigorite indicate volume contraction during this reaction42. These results indicate that carbonation of mantle wedge potentially has effects on the behavior of subduction zone thrusts. However, our understanding of carbonation processes in the mantle wedge is limited by a lack of well-characterized examples from ancient exhumed subduction zones. Carbonated serpentinites from the high-pressure (HP) Sanbagawa metamorphic belt in Japan, which represents part of an exhumed Cretaceous subduction zone, provide an unique opportunity to understand the mechanisms of carbonation within a mantle wedge corner under P–T conditions similar to those at active ETS is reported.

Results and discussion

Carbonation of serpentinite associated with brittle fracturing

The Sanbagawa belt is a HP metamorphic belt that extends ~800 km along the Median Tectonic Line from the Kanto Mountains in the east to Kyushu in the west along Japan (Supplementary Fig. 1). It is composed mainly of metasediments and metabasalts that formed during Cretaceous subduction of an oceanic plate. The metamorphic belt also contains meter- to kilometer-scale ultramafic blocks including mantle peridotites, serpentinites, and tremolite-rich rocks42. The mineral compositions and restricted distribution of these ultramafic blocks to regions higher than chlorite zone indicate that they originated in the mantle wedge4,42,43. The Higuchi serpentinite body (15 × 8 m; Fig. 1a) is located in the Kanto Mountains near the boundary between the garnet and chlorite zones (36°07’00.0″N 139°07’00.0″E; Supplementary Fig. 1). Raman analysis of carbonaceous materials indicates peak temperatures of 400–450 °C in this area44, and mineral phase equilibria suggest peak pressures of ~0.5–0.9 GPa45. The long axis of the serpentinite body is subparallel to a mineral lineation in the surrounding pelitic schists. The Higuchi body is composed of massive or foliated antigorite (Fig. 1b, c) that is cut by dense networks of multi-generational carbonate(s) + talc veins (Fig. 1a–e and Supplementary Fig. 2), including magnesite (Fig. 1c, d), dolomite (Fig. 1a, b), and dolomite + calcite (Fig. 1e). The carbonate veins propagate from the margin to the center of the body in a branching network (Supplementary Fig. 2). Along contacts with serpentinite (Fig. 1f), the pelitic schists are progressively converted to layers of chlorite rock ~50 cm wide that preserve bands containing primary metamorphic graphite, and then to lenses of actionite + chlorite schist up to ~30 cm wide (Supplementary Fig. 3).

Blocks of massive serpentinite (Fig. 1b) are composed of randomly oriented antigorite grains (Fig. 2a, b) with minor amounts of Cr-rich spinel. Olivine, pyroxenes, and brucite are absent. Cr-rich spinel is commonly altered to magnesiocromite (Fig. 2c and Supplementary Table 1), but some Cr-rich spinel grains in the serpentinite and actinolite–chlorite schists retain unaltered cores with X_Cr (Cr/(Cr+Al)) = 0.52–0.58 and X_Mg (Mg/(Mg+Fe)) = 0.55–0.64. Such depleted spinel compositions in the Higuchi serpentinite are similar to those in forearc
peridotites and those of other ultramafic bodies in the Sanbagawa belt (Fig. 2c). Carbonate veins in the Higuchi body are composed mainly of dolomite and magnesite, with lesser amounts of calcite. Magnesite commonly occurs as patches 0.2–2.0 mm in size within antigorite blocks (Fig. 2a, d, e), often accompanied by networks of talc veins <1 mm thick. Magnesite–talc layers also occur along foliation surfaces (Fig. 2a), and infill the spaces between asymmetric antigorite blocks produced by brittle shear deformation (Fig. 2e). Dolomite + talc veins are the most distinct veins in the serpentinite body because they are relatively thick (>2 cm) and can be >3 m long (Figs. 1b, c and 2f). Talc occurs along the margins of these veins (Fig. 2f). Some thick dolomite veins show a layered structure including enclaves of serpentinite (Fig. 1b, c, e). The asymmetry of serpentinite fragments, the presence of asymmetric folds (Fig. 1c), and the presence of several layers composed of dynamically recrystallized dolomite grains cutting coarse-grained dolomite veins (Fig. 2g), indicate that vein formation and development of localized shear zones was a repetitive process. In some relatively thick veins, euhedral dolomite crystals grew in the center of the veins, and anhedral calcite crystals filled the intervening pore spaces (Fig. 2b). The dolomite crystals in contact with calcite have higher-Fe rims (Supplementary Fig. 4), suggesting that such dolomite rims were in equilibrium with calcite (Supplementary Table 1). Application of calcite–dolomite solvus thermometry to these veins indicates a carbonation temperature of 380–400 °C (Supplementary Fig. 4).

Sources and compositions of carbonic fluids. Carbonic fluids in subduction zones are commonly sourced from carbonates in seafloor sediments, hydrothermal alteration of basaltic oceanic crust, or organic materials in sediments. In the Sanbagawa belt, the rare marbles have δ13C values of 0.4–2.8‰, typical of marine limestones (Fig. 2i). The stable isotope compositions of calcite in pelitic and basic schists, and related veins, have relatively constant δ18O values (15–17‰) and a large variation in δ13C (−12–2‰), reflecting multiple sources of CO2 including oxidation of in situ biogenic carbonaceous material and
Fig. 2 Microstructure and chemistry of minerals in the Higuchi serpentinite body. a Photomicrograph (crossed polarized light) showing massive antigorite and magnesite patches associated with talc vein networks. b Detail of antigorite showing random grain orientations. c, d Serpentinitized peridotites in the Sanbagawa belt, central Shikoku (references therein); SH Shiraga body, HA Higashi Akashi body, IM Imomo body. d Mineral map of magnesite patches rimed by talc. Location of map shown in a. e Fissural-vein zones within the Sanbagawa schists. f Magnesite patches surrounded by talc in the Higuchi serpentinite body. g BSE image of a thick dolomite vein. h Photomicrograph (crossed polarized light) showing massive antigorite crystals with bright rims along the margin of the vein, and anhedral calcite occurs in the center of the vein. The compositional profile of dolomite along the plane A–B is shown in Supplementary Fig. 3. i Isotopic compositions (δ13C, δ18O) of carbonates (magnesite, dolomite, and calcite) in veins from the Higuchi serpentinite, compared with marbles from central Shikoku and the compositions of calcite in basic schists and pelitic schists, and associated veins in the Nagatoro area.

Possible tectonic setting of carbonation and serpentinitization.

Geological field relationships, including the chemical compositions and P–T conditions recorded by HP metamorphic rocks, indicate that the Higuchi body experienced serpentinitization and carbonation at depths of 20–35 km, comparable to conditions in the corner of the mantle wedge in active warm subduction zones such as the Nankai subduction zone in SW Japan (Fig. 3a). Our observations suggest that the toe of the forearc mantle was initially serpentinitized without macroscopic fracturing (Fig. 3b), followed by local carbonation associated with intense fracturing (Fig. 3c). The metasomatic sequences observed in the Higuchi body progress from the pelitic schists to the interior of the serpentinites as follows: Chl (after pelitic schist)/Act + Chl/Cal + Dol/Dol + Talc/Mgs + Talc (after serpentinite) (Fig. 3c). Mass balance analyses reveal that chloritization of the pelitic schists was characterized by gains in MgO and FeO, and losses of SiO2 and H2O at nearly constant Al2O3, resulting in an overall ~35% reduction in solid volume (Supplementary Table 2 and Supplementary Fig. 5). In contrast, the quantitative mass balance analysis of the carbonation of the serpentinite body is difficult due to the heterogeneous distribution of carbonate veins, the carbonation reactions were characterized by the formation of carbonates (magnesite, dolomite, or calcite) + talc at the expense of antigorite, and accompanied by gains in CO2, SiO2, and CaO, and losses of H2O and MgO (Fig. 3c).

metrical processes. In contrast, carbonates in the Higuchi serpentinite body show a relatively narrow range of δ13C (~10.3%o to ~9.3%o), with the exception of one dolomite sample (~7.6%o), and a wide range of δ18O between 17.0%o and 20.2%o. These C–O isotope data indicate that (1) CO2 in the fluids that carbonated the Higuchi serpentinite body was not derived from limestones, but from the degradation of organic material or carbonates derived from methanotrophic processes within the pelites, and (2) carbonic fluids were probably mixed with H2O produced by dehydration of serpentinite during carbonation reactions, such as

\[
\begin{align*}
\text{MgsSi}_2\text{O}_3\text{(OH)}_2 + 48\text{CO}_2(\text{aq}) & \rightarrow 4\text{MgCO}_3 + 34\text{SiO}_2 + 3\text{H}_2\text{O}, \\
\text{Antigorite} & = \text{Magnesite} + \text{Quartz}.
\end{align*}
\]

\[
\begin{align*}
2\text{MgsSi}_2\text{O}_3\text{(OH)}_2 + 45\text{CO}_2(\text{aq}) & \rightarrow 45\text{MgCO}_3 + 17\text{MgsSi}_2\text{O}_3\text{(OH)}_2 + 43\text{H}_2\text{O}, \\
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Metamorphic processes. In contrast, carbonates in the Higuchi serpentinite body show a relatively narrow range of δ13C (~10.3%o to ~9.3%o), with the exception of one dolomite sample (~7.6%o), and a wide range of δ18O between 17.0%o and 20.2%o. These C–O isotope data indicate that (1) CO2 in the fluids that carbonated the Higuchi serpentinite body was not derived from limestones, but from the degradation of organic material or carbonates derived from methanotrophic processes within the pelites, and (2) carbonic fluids were probably mixed with H2O produced by dehydration of serpentinite during carbonation reactions, such as

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Progress of carbonation assisted by reaction-induced fracturing and Mg-mobility. We conducted thermodynamic modeling of the interactions between pelite-derived fluids and serpentinite at 400 °C and 0.5 GPa with variable fluid–rock ratios (F/R ratio; see Methods section). The initial fluids were assumed to be in equilibrium with the graphite-bearing pelitic schists at various oxygen fugacities, $f_{O_2}$ (Supplementary Fig. 6). Given graphite saturated fluids, the atomic fraction of oxygen to oxygen + hydrogen in initial fluid, $X_O$, is determined for each $f_{O_2}$.

At 400 °C and 0.5 GPa, graphite-bearing assemblages appear at high $F/R$ ratios when antigorite reacts with relatively reducing fluids (Fig. 4a). This is because the solubility of graphite decreases slightly with the addition of antigorite to reducing fluids, as the precipitation of clinopyroxene and tremolite reduces the concentration of Ca-bearing carbonic aqueous complexes, such as Ca(HCO$_3$)$^+$, Ca(HCO$_3$)$^2$+, and CaCO$_3$$^aq$. In cases with initial fluids around the quartz–talc–magnetite (QFM) buffer ($f_{O_2} = -28.1$, $X_O = 0.337$), relatively common metasomatic minerals (tremolite, chlorite, talc)$^{12}$ appear along the interfaces between ultramafic rocks and metasediments at log $[F/R]$ of 1.5–2.5.

Typical carbonate-mineral assemblages are found in cases with initial fluids at around QFM + 0.3 ($f_{O_2} = -27.8$, $X_O = 0.344$; Fig. 4a, b). At log $[F/R] > -2.5$, plagioclase, calcite, chlorite, and quartz appear, which are typical minerals in veins within the Sanbagawa pelitic schists$^{34}$. With an increase in the proportion of antigorite, the mineral assemblage evolves as follows: Chl ± Qtz ± Cpx/Chl ± Tr/Cal ± Talc/Dol ± Talc/Mgs ± Talc/Mgs + Atg (Fig. 4b, c). Such a mineralogical sequence reflects the fluid-dominated system at the boundary of the serpentinite body and close to the large veins, and the rock-dominated system in the interior of the serpentinite body with a fine vein network (Fig. 4c) observed within the Higuchi serpentinite body (Figs. 1–2). At log $[F/R] < -2.0$, $H_2O$ is released by tremolite, and talc and carbonates form at the expense of antigorite, while $CO_2$ is consumed (Fig. 4d). Carbonaceous material in sedimentary rocks is initially poorly crystalline, and its crystallinity increases during prograde metamorphism in subduction zones. Therefore, the disordered graphite exists in the metapelites around the Higuchi body$^{14}$. In the presence of disordered graphite, the $CO_2$ concentration in the input solution could have been greater than those estimated by our thermodynamic calculations (Fig. 4d), which assumed the presence of crystalline graphite$^{32}$. This could result in the formation of larger amounts of carbonates at the same $f_{O_2}$ conditions in the initial solution.

With a decrease in the $F/R$ ratio (log $[F/R] < 1.5$; i.e., representative of the interior of the serpentinite body), carbonates + talc form by consumption of antigorite. pH increases and $f_{O_2}$ slightly decreases (Supplementary Fig. 7), as reported in previous studies$^{35,36,55}$. Si is the dominant component in the initial fluid, as it is saturated with quartz (Fig. 4e). The aqueous $CO_2$ species dominantly exists as the MgSiO$_3$(OH)$_2$(HCO$_3$)$^+$ complex (Supplementary Fig. 7). Such effects of Si$_2O_3$ on the enhancement of carbon solubility have been inferred from dissolution experiments on forsterite + enstatite + graphite$^{34}$. As the amount of antigorite increases, the concentration of Si decreases and the concentration of Mg increases (Fig. 4e). For example, at log $[F/R] = 1.0$, the overall mass balance for the carbonation of serpentinite is:

$$\begin{align*}
&Mgs_6Si_8O_{24}(OH)_{28} + 1.82SiO_2(aq) + 0.07Al_2O_3(aq) + 0.22CaO(aq) + 12.99CO_2(aq) \\
&\rightarrow 8.90Mg_5Si_3O_{10}(OH)_{2} + 12.54MgCO_3 + 0.22MgCaCO_3 + 0.07MgAl_2SiO_5(OH)_7 + \text{Talc} + \text{Dolomite} + \text{Magnesite} + \text{MgCl}_2 + 8.18\text{H}_2\text{O}.
\end{align*}$$

(3)

In reaction 3, a small amount of chlorite is formed. Chlorite is not found in the Higuchi serpentinite, but Al-rich antigorite often occurs with talc. Interestingly, the Mg concentration at low log $[F/R]$ (<1.5), which exists dominantly as Mg(OH)$_2$$^aq$ (Supplementary Fig. 7), is higher than the Si concentration in the initial fluid, implying relatively high mobility of Mg in the mantle wedge. Moreover, at low $F/R$ where talc + carbonates are formed (Fig. 4f), the solid volume decreases ($V_{\text{solid}}/V_{\text{solid,0}} = 0.7–1.0$), whereas the total volume (solid + fluid) increases ($V_{\text{total}}/V_{\text{total,0}} = 1.000–1.004$). Observations from recent laboratory experiments conducted under forearc mantle conditions$^{40}$ support our modeling and field observations, suggesting that the progressive formation of magnesite + talc is associated with a solid volume decrease. Although the fluid-mineral equilibria and volume changes were computed for isobaric condition (Fig. 4f), the values of $V_{\text{total}}/V_{\text{total,0}} > 1$ at low $F/R$ suggest that carbonation reactions of serpentinized mantle tend to result in a fluid pressure rise when the system is undrained.

Fracturing induced by volume-changing reactions. To understand the effects of the solid volume change and fluid pressure increase on fracturing, we conducted numerical simulations of coupled fracturing, reaction, fluid flow, and element diffusion using a distinct element method$^{36}$ (see Methods section). We consider a simple metasomatic dehydration reaction between a serpentinite body and a matrix of pelitic schist (Fig. 5a), in the cases of dilation (Fig. 5b) and contraction (Fig. 5c). In the model, the reaction proceeds along the margins and fractures within the serpentinite body in response to diffusive flux of metasomatic agents (i.e., $CO_2$ species or silica), which is saturated in the pelitic
Fig. 4 Results of thermodynamic calculations of the interaction between pelitic-schist-derived fluids and antigorite at 400 °C and 0.5 GPa. 

- **a** Stable mineral assemblage as a function of fluid/rock mass ratio (F/R) and oxygen fugacity, fO2, and the atomic fraction of oxygen to oxygen + hydration, XO, of the initial solution. Pale blue and pink shaded regions indicate carbonate- and graphite-bearing assemblages, respectively. Red dashed lines indicate QFM + 0 (XO = 0.337) and QFM + 0.3 (XO = 0.344) of the initial solution.

- **b-f** Results in the case of log fO2 = -27.8 (QFM + 0.3, XO = 0.344) of the initial solution as a function of log [F/R]. 

In both cases of dilation and contraction, fluid pressure increases within the serpentinite body, but different fracture patterns are produced depending on the volume change. In the case of dilation, radial cracks develop preferentially within the surrounding matrix (Fig. 5b, d and Supplementary Fig. 10a). In contrast, fracture networks are preferentially developed within the serpentinite body in the case of contraction (Fig. 5c, d and Supplementary Fig. 10b), and the fracture networks develop from the margin with branching-out structure, which shows a similar geometry as the carbonate veins in the Higuchi body (Fig. 1a–e and Supplementary Fig. 2). These contrasting fracture patterns are consistent with previous numerical simulations and laboratory experiments. Similar fracture patterns are also reproduced (Supplementary Fig. 11) even when fracturing is simulated in models of metasomatic reaction with dilation or contraction but without fluid flow and dehydration. The thermodynamic calculations (Fig. 4) and DEM simulations (Fig. 5) indicate that volume contraction is likely to be the main cause of fracturing during carbonation. Euhedral dolomite grains that are interpreted to have grown in open space (Fig. 2i) indicate that volume contraction is likely to be the main cause of fracturing during carbonation. Euhedral dolomite grains in the Sanbagawa belt are estimated to be 2.1 × 10^{-5} m² under a confining pressure of 200 MPa, and the porosity of the pelitic schist is low and similar to that of chlorite schist in subduction zones (0.01%–0.2%). Such low porosity and permeability in the pelitic schist and the relatively high reaction rate of carbonation with dehydration (several [tens of] percent of carbonate from an antigorite block in a few days) could result in fluid overpressure within the serpentinite body, as discussed in...
dehydration of serpentine\textsuperscript{60}. The volume contraction produces tensile cracks at an isotropic effective confining stress (Fig. 5), but mechanical instabilities associated with volume changes and fluid overpressure during reaction can trigger earthquake ruptures at high differential stresses\textsuperscript{60,63}.

Consequences of heterogeneous and episodic carbonation in the mantle wedge. In the Sanbagawa belt, carbonation of some ultramafic blocks has occurred\textsuperscript{47} but the distribution and extent of carbonation reactions are restricted\textsuperscript{40,47}. In the Higuchi body, carbonates were not formed during the initial stages of serpentinization (to form antigorite). These features suggest that in contrast to the relatively homogeneous serpentinization process (Fig. 3b), carbonation in the mantle wedge may involve rupturing that is heterogeneous in time and space (Fig. 3c). The reactions involving carbonic fluids are influenced by redox conditions. It is well known that peridotite has a high reducing potential\textsuperscript{64,65} but the redox conditions in a fully serpentinized body could be modified by fluid–rock interactions after serpentinization\textsuperscript{66}. In the case of the Higuchi body, carbonation did not occur in the initial stage of serpentinization (massive antigorite; Fig. 2a, b), and chloritized pelitic schists at the boundary were not significantly depleted in graphite (Supplementary Figs. 3a and 5). Therefore, it is unlikely that the CO\textsubscript{2} fluid was produced only near the serpentinite body under oxidizing conditions. Based on analysis of the Higuchi body, we infer that carbonation of the mantle wedge can be induced by episodic ingress of carbonic fluids that may be created by oxidation of carbonaceous materials with fluids passing through subducted oxidized layers, including hematite-bearing mafic schists and bedded manganese deposits\textsuperscript{67,68}. In addition, we emphasize that once carbonic fluids reach the mantle wedge, carbonation can proceed in a self-promoting way via positive feedbacks between the reaction, volume contraction, fracturing, and transport of elements and CO\textsubscript{2}–H\textsubscript{2}O fluids (Figs. 3–5)\textsuperscript{40,56}.

In the Nankai subduction zone in Shikoku, SW Japan, ETS is observed at the slab–mantle interface near the corner of the mantle wedge\textsuperscript{20–23,69}. The frictional behavior of serpentine, as well as metasomatic products such as talc, chlorite, and tremolite, is characterized by stable slip related to strain hardening\textsuperscript{70}. A notable feature of carbonation within the Higuchi body is that networks of millimeter- to meter-scale carbonate–talc veins developed during the carbonation of serpentinized mantle (Figs. 1–2 and Supplementary Fig. 2). The total volume increase (fluid + solid) suggested by the thermodynamic modeling of carbonation (Fig. 4f) might cause non-double coupled earthquakes, as reported in swarm seismicity in volcanic zones\textsuperscript{71}. However, the signal of ETS is consistent with shear slip on the plate interface\textsuperscript{69}, and non-double coupled components are not clear due to the large signal-to-noise ratio. The high fluid pressure observed in the Higuchi body (Fig. 2) and suggested by the modeling (Fig. 4f) is consistent with high $V'_{\text{fl}}/V_s$ ratios associated with the ETS region\textsuperscript{21,22}. The DEM modeling reveals that volume contraction in the presence of high fluid pressures tends to generate tensile fractures (Fig. 5 and Supplementary Fig. 10b), which may subsequently transform (or develop) into shear fractures under differential stress. The brittle shear failures observed in thin-sections and outcrops (Figs. 1b, c and 2e) are consistent with the mechanism of low-frequency earthquakes related to shear slip on the plate interface\textsuperscript{21,69}. Following sealing of void spaces by carbonates, localized shear is concentrated within the talc-rich layers (Figs. 1b and 2a, e) and dolomite veins (Figs. 1c and 2f). We speculate that this kind of repeated brittle failure, followed by viscous flow, may represent an analog for the ETS that is observed within the relatively cold nose of the mantle wedge.

Methods

Measurements of stable isotope compositions of carbonate minerals. The chemical compositions of minerals were analyzed using an electron microprobe analyzer (EPMA, JEOI8200) at Tohoku University. The acceleration voltage was 15 kV, and the current was 12 nA or 120 nA for quantitative analyses and elemental mapping, respectively. Identification of serpentine and other minerals was performed using a Raman spectrometer (Horiba XploroRa) equipped with an Olympus BX51 microscope at Tohoku University.
Oxygen ($^{18}$O) and carbon ($^{13}$C) isotope analyses were conducted on selected carbonate samples from the Higuchi serpentinite body. For comparison, we also analyzed the stable isotope compositions of marble samples from the Sanbagawa belt in central Shikoku. Samples were extracted from cut and polished slabs using a sharp knife, and then stained with Alizarin red-S to distinguish between calcite and dolomite. Staining with Alizarin red-S does not affect the C and O isotope ratios. Sample powders for C-O isotope analyses were taken from different portions of each sample. The carbonate mineral (dolomite, magnesite, or calcite) powders were placed into small stainless steel thimbles and dropped into a reaction vessel containing pyrophosphoric acid at 60 °C (calcite) or 100 °C (for dolomite and magnesite) in vacuum to produce CO2 gas. Released CO2 gas was cleaned to remove impurities like H2O by using pentane slush and collected by using liquid nitrogen cold traps. Stable isotope measurements were carried out on a Thermo Finnigan MAT-253 mass spectrometer at Niigata University. Results are reported in conventional per mil (%) notation with respect to V-SMOW (Vienna-Standard Mean Ocean Water) for oxygen and V-PDB (Vienna-Belemnite Belemnite) for carbon.

Thermodynamic model of fluid–rock interaction. Thermodynamic calculations were carried out in the system Na-K-Ca–Fe–Mg-Al-Si–Cl–H-O with the Deep Earth Water (DEW) model3,4,7,8 and software EQ3/6 with a modified Berman thermodynamic dataset9. This updated thermodynamic dataset includes H2O, CO2, H2CO3, and various complexes related to boric acid (NaH2BO3, Ca(H2BO3), and MgH2BO3). For this reason, thermodynamic calculations are not restricted to the H2O-rich system but also model CO2-rich fluids involving carbonation10. We treated solid solutions as ideal mixing between Mg and Fe endmembers for chlorite, talc, tremolite, biotite, and clinopyroxene, and between albite and anorthite for plagioclase. We first created an input solution using EQ3, in equilibrium with the observed mineral assemblage in the pelitic schist muscovite-chlorite (XMg = 0.6) + quartz + albite + chloritoid + calcite + graphite, at 400 °C and 0.5 GPa11. This mineral assemblage represents the most likely fluid source or the metasomatic and carbonation reactions within the serpentinite. The pressure of carbonation in the Higuchi serpentinite was not determined, but probably ranges between 0.5 and 0.9 GPa based on the P–T–fO2 conditions in the chlorite and garnet zones12. At 400 °C, there is no miscibility of CO2 and H2O below 1 GPa13. The log oxygen fugacity of the input solutions, log$\delta$ (fluid), ranged from −29.0 to −27.5, corresponding to QFM (deviation from quartz-fayalite-magnetite buffer) from −0.8 to +0.7 in log units14. Based on the compositions of each initial solution calculated by EQ3, Xo is obtained as follows:

$$Xo = \frac{m_1}{m_2^* + m_3^*}$$

(4)

where $m_1$ and $m_2$ are the number of moles of oxygen and hydrogen in the fluids, respectively15. The log$\delta$ (max) range of the initial solutions corresponds to Xo from 0.318 to 0.354. EQ6 was then used to model the interactions (thermodynamic equilibrium) between the input solution and serpentinite composed of 100% antigorite (Fig. 4).

We calculated fluid/rock mass ratios from −2.0 to 4.0. To create the stable mineral assemblage at various F/R and fO2 conditions for the input solution (Fig. 4a and Supplementary Fig. 6), a shell script was written to automatically generate EQ3/6 runs inputting the fO2 conditions, and the output files generated by EQ6 were further processed with an author-generated MATLAB® script.

The changes in CO2 and H2O during the reactions (Fig. 4d) are calculated by determining changes in hydrous minerals and carbonates. The volume change ratio of the solids ($\frac{V_{solid/initial}}{V_{solid}}$, Fig. 4f) was calculated by using the volumes of product minerals and consumed antigorite. The volume change ratio of solid and fluids ($\frac{V_{solid/initial}}{V_{solid}}$, Fig. 4f) was calculated by the volumes of product minerals, consumed antigorite, and changes in the amount of fluid. The molar volume of fluids was obtained based on the sum of the concentration of carbonic species. With decreasing log F/R, the $X_{CO2}$ values decrease from 2.30 × 10$^{-2}$ to 1.88 × 10$^{-2}$. We also undertook the same calculation at 400 °C and 1.0 GPa (Supplementary Fig. 8). We found that the topography of the stable mineral assemblage in a plot of log$\delta$ (fO2) vs. log F/R is largely similar to the case at 400 °C and 0.5 GPa (Fig. 4a), except that albite is stable instead of calcite. The chemistry of the initial solution calculated by EQ3 is also largely consistent with that calculated by PerpleX version 6.1.536 with thermodynamic data of Holland and Powell17 (Supplementary Fig. 9).

Distinct element method to model metasomatic dehydration reactions. We conducted two-dimensional distinct-element numerical simulations to investigate fracture patterns induced by volume-changing dehydration reactions, following the methods of Okamoto & Shimizu35 with slight modifications to incorporate element diffusion. Okamoto & Shimizu35 treated coupled processes of reaction (dehydration/ hydration), fluid flow, and fracturing. The model consists of an aggregate of circular elements connected by elastic bonds. When the external force exceeds the tensile or shear strength of the bond, the bond is broken to form a microcrack. To treat fluid flow, we calculate the fluid pressure in each domain, which is defined by the nearest surrounding connected elements. The fluid flow in a channel is calculated by the Poiseuille equation and includes the crack aperture ($\omega$), fluid viscosity ($\mu$), the length of the flow channel, and the fluid pressure gradient between adjacent domains ($\Delta P$). Okamoto & Shimizu35 considered a simple hydration/dehydration reaction as Mineral A + H2O → Mineral B, and the reaction rate is assumed to be a linear function of fluid pressure. They showed that contrasting fracture patterns are produced in response to solid volume changes rather than fluid pressure as similar to the other studies56–59. Here, as a simplification of the carbonation of serpentinite, we consider a simple metasomatic dehydration reaction:

Mineral A + Aqueous species S → Mineral B + H2O

(5)

where aqueous species S represents metasomatic agents such as CO2 species and SiO2. The reaction is characterized by the volume change factor (the volumetric ratio of 100% reacted particle to unreacted particle), the ratio of the changes in fluid and particle volume (fluid volume factor), and the ratio of the changes in the amount of species S with respect to the particle volume change (solute factor). For this study, we used volume factors of 1.1 (dilation) or 0.9 (contraction), a fluid factor of −0.1, and a solute factor of 1.0. The reaction rate, Z, is defined as a function of the concentration of Ca6 as follows:

$$Z = Z_{max}(1 - \frac{C_{min} - C_0}{C_{max} - C_0})$$

(6)

$C_{max}$ and $C_{min}$ represent maximum and minimum concentrations of the species S in the system: the reaction rate is greatest ($Z_{max}$) at $C = C_{max}$ and the reaction stops at $C = C_{min}$. In addition to advective transport with H2O, we consider diffusional transport of aqueous species S as a function of the concentration gradient of S in each domain.

The values of the parameters used in this study are summarized in Supplementary Table 3. This study used a 10 x 10 m square rock model that contains 4357 particles with diameters of 50–100 mm. This rock specimen initially contains a reactive mineral domain composed of antigorite, and contrasting fracture patterns are produced in response to solid volume changes rather than fluid pressure as similar to the other studies56–59. Here, we consider that the species S is saturated within the non-reactive matrix. The physical properties (particle density, $\rho$, and Young’s modulus, $E$) of the matrix material are based on quartz ($\rho = 2600 \text{ kg/m}^3$; $E = 140 \text{ GPa}$), whereas the reactive mineral properties change from antigorite ($\rho = 2600 \text{ kg/m}^3$; $E = 115 \text{ GPa}$) to a mixture of dolomite (95%) and talc (5%) ($\rho = 2830 \text{ kg/m}^3$; $E = 110 \text{ GPa}$), following the data of Mavko et al.82 and Abers & Hacker83 (Supplementary Table 3). There are no experimental data on the tensile and shear strengths of these minerals, but the tensile strength of rock typically ranges from ~1 to 10 MPa, and compressive strengths are typically ~10 times the tensile strengths84. Here, we set the tensile and shear strengths in the rock model to be 10 and 100 MPa, respectively, regardless of the minerals in the model. Based on these strength data, we performed preliminary simulations of uniaxial compression and tension tests to adjust microscopic input parameters85, and decided to use a tensile spring strength of 30 MPa and a shear spring strength of 118 MPa. The effective confining pressure was set to be 1 MPa. The initial and fluid pressures outside the rock model were set to $P_{min}$ and when dehydration reaction proceeds fluid pressure, $P_{\text{ic}}$ inside the rock increases and fluid flows toward outside. The fluid physical properties (viscosity of $1.0 \times 10^{-3}$ Pas and bulk modulus of 3.5 GPa) were assumed to be the same as those at atmospheric pressures of ~400 °C and pressures of 0.5 GPa. The concentration of species S, $C_0$, is assumed to be a maximum value ($C_{max} = 1.0$) in the non-reactive matrix (saturated), and $C_0$ in the reactive mineral domain is set to be $C_{min} (=0.3)$ at the initial stage. The apparent diffusion coefficient ($\approx$ diffusion coefficient/average particle size) was set to $0.5 \times 10^{-3} \text{ m}^2/\text{s}$ in unbroken rocks, and $10^{-4} \text{ m}^2/\text{s}$ along fractures. As the diffusive flux of species is large with respect to the fluid flow, the concentration of $S$ is nearly equal to $C_{max}$.

Reporting summary. Further information on research design is available in the Nature Research Reporting Summary linked to this article.

Data availability

The data of this study are available in methods and supplementary tables. The input and output files for EQ3 and EQ6 for representative cases (Fig. 4), and animations of the DEM simulation results are available in the online repository (https://doi.org/10.6084/m9.15.8650).

Code availability

The DEM code used in this study is available from the corresponding author upon request with the approval of A.O. and H.S.

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Author contributions
A.O., R.O., K.Y., and M.U. carried out field work. A.O. carried out the petrological analyses. R.O. carried out the thermodynamic calculations on fluid–rock interaction. M.U. performed mass balance analyses. K.Y. and H.S. developed the DEM model and carried out simulations. M.S. and K.Y. performed the isotope analyses of carbonates. A.O. wrote the paper with inputs from all authors.

Competing interests
The authors declare no competing interests.

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