



Abiotic methane synthesis and serpentinization in olivine-hosted fluid inclusions

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The conditions of methane (CH₄) formation in olivine-hosted secondary fluid inclusions and their prevalence in peridotite and gabbroic rocks from a wide range of geological settings were assessed using confocal Raman spectroscopy, optical and scanning electron microscopy, electron microprobe analysis, and thermodynamic modeling. Detailed examination of 160 samples from ultraslow- to fast-spreading midocean ridges, subduction zones, and ophiolites revealed that hydrogen (H₂) and CH₄ formation linked to serpentinization within olivine-hosted secondary fluid inclusions is a widespread process. Fluid inclusion contents are dominated by serpentine, brucite, and magnetite, as well as CH_{4(g)} and H_{2(g)} in varying proportions, consistent with serpentinization under strongly reducing, closed-system conditions. Thermodynamic constraints indicate that aqueous fluids entering the upper mantle or lower oceanic crust are trapped in olivine as secondary fluid inclusions at temperatures higher than ~400 °C. When temperatures decrease below ~340 °C, serpentinization of olivine lining the walls of the fluid inclusions leads to a near-quantitative consumption of trapped liquid H₂O. The generation of molecular H₂ through precipitation of Fe(III)-rich daughter minerals results in conditions that are conducive to the reduction of inorganic carbon and the formation of CH₄. Once formed, CH_{4(g)} and H_{2(g)} can be stored over geological timescales until extracted by dissolution or fracturing of the olivine host. Fluid inclusions represent a widespread and significant source of abiotic CH₄ and H₂ in submarine and subaerial vent systems on Earth, and possibly elsewhere in the solar system.

abiotic methane | fluid inclusions | serpentinization | methane seeps | carbon cycling

The formation of molecular hydrogen (H₂) and abiotic hydrocarbons such as methane (CH₄) has far-reaching implications for our understanding of the deep Earth carbon cycle, as well as the origin and maintenance of life on Earth and beyond. Elevated concentrations of H₂ and CH₄ are associated with the hydrous alteration of olivine-rich (ultramafic) rocks in many natural environments, a process that entails a number of redox-dependent dissolution–precipitation reactions collectively known as serpentinization. Large quantities of H₂ are generated during aqueous oxidation of ferrous iron-bearing minerals which results in the reduction of dissolved inorganic carbon ($\sum \text{CO}_2 = \text{CO}_{2(aq)} + \text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^{2-}$). Due to its important roles in a broad array of biogeochemical processes, few aspects of deep-sea hydrothermal vent systems and alkaline springs and gas seeps on land have attracted more attention than the origin of abiotic CH₄ (1–5). Field observations have revealed that the abundance of abiotic CH₄ in hydrothermal systems hosted in mafic rocks (basalt, diabase, gabbro) is substantially lower than in hydrothermal systems hosted in ultramafic rocks (peridotite or peridotite plus gabbro), but the pathways of abiotic CH₄ synthesis have remained elusive. Recently, McDermott et al. (3) used carbon isotopic and mass balance constraints to demonstrate that $\sum \text{CO}_2$ reduction by H₂ does not yield CH₄ during convection of hydrothermal fluids at the Von Damm hydrothermal field, suggesting that abiotic CH₄ formation and convective seawater circulation are decoupled. This challenged the paradigm of significant abiotic CH₄ formation during active fluid circulation and led to the suggestion that abiotic CH₄ observed in

deep-sea hydrothermal fluids associated with ultramafic rocks may be leached from fluid inclusions (3, 6–8). Many important questions remain regarding fluid inclusion prevalence, formation, internal fluid–mineral interaction, and their contributions of CH₄ to venting fluids and global reservoirs. Moreover, because fluid inclusions may form in olivine-rich rocks that interact with water on celestial bodies elsewhere in our solar system, their formation may have key implications for the maintenance of microbial life beyond Earth.

Here we examined the chemical and mineralogical composition of fluid inclusions in olivine-bearing gabbros and partially serpentinized peridotites from ultraslow-, slow-, and fast-spreading midocean ridges, a backarc basin, subduction zone forearcs, and ophiolites (Fig. 1 and *SI Appendix*, Table S1). We assessed the distribution and composition of secondary fluid inclusions in olivine by means of confocal Raman spectroscopy, scanning electron microscopy, transmitted and reflected light microscopy, and electron microprobe analysis. Complementing these efforts, we used thermodynamic reaction path models to assess the geochemical environments present within the inclusions during fluid entrapment, serpentinization, and CH₄ formation.

Methane Abundance in Oceanic Peridotite and Gabbro

Examination of gabbro ($n = 43$) and peridotite ($n = 117$) in thin sections with relict olivine revealed the presence of fluid inclusions in rocks from each of the field locations shown in Fig. 1. All of the olivine-bearing gabbro samples and 77% of the peridotite samples contain fluid inclusions hosted in olivine. Image analyses of some of the most inclusion-rich samples revealed more than 3×10^6 inclusions per cm³. Inclusions vary in size from <100 nm to ~30 μm in diameter and are heterogeneously distributed on a millimeter to centimeter scale (Figs. 2 and 3 and *SI Appendix*,

Significance

Our findings highlight the ubiquitous occurrence of methane (CH₄)-rich fluid inclusions in olivine-bearing rocks that, collectively, may constitute one of the largest reservoirs of abiotic CH₄ on Earth. Because serpentinization in olivine-hosted fluid inclusions takes place in isolation from the surrounding rock, hydrogen (H₂) and CH₄ can form in any rock type containing olivine that hosts aqueous fluid inclusions, including those that do not undergo serpentinization on a macroscopic scale. Serpentinization and associated CH₄ formation within olivine-hosted fluid inclusions has likely supplied microbial ecosystems with abiotic CH₄ throughout most of Earth's history and may be a source of H₂ and CH₄ on other planetary bodies in our solar system, even those where liquid water is no longer present.

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Figs. S1, S3, and S4). Most inclusions occur along planes, which indicate a secondary origin via annealing of fluid-filled fractures in the olivine host (9, 10). With the exception of 3 sites, i.e., Hess Deep, the Romanche Fracture Zone, and the Mid-Atlantic Ridge Kane Fracture Zone Area (MARK) which do not contain detectable CH_4 in olivine-hosted fluid inclusions despite being rich in H_2 , olivine-hosted fluid inclusions from all other sites examined in this study contain $\text{CH}_{4(g)}$ or $\text{CH}_{4(g)}$ and $\text{H}_{2(g)}$ (Figs. 1 and 3 and *SI Appendix*, Figs. S1 and S2 and Table S1). The partial pressure of $\text{CH}_{4(g)}$ within olivine-hosted fluid inclusions determined using empirical calibrations of the Raman shifts of $\text{CH}_{4(g)}$ (11) (*SI Appendix*, Table S1) are 0.4 to 55 MPa, with an average of 11.5 MPa. Using the ideal gas law and the assumption that fluid inclusions are spherical, we calculated that an inclusion with a diameter of 10 μm contains 8.4×10^{-5} to 1.2×10^{-2} nmol $\text{CH}_{4(g)}$.

The $\text{CH}_{4(g)}$ content of individual fluid inclusions can be used in conjunction with their abundance to estimate the $\text{CH}_{4(g)}$ content of olivine-rich rocks. A rock containing 10^5 inclusions per cm^3 would contain 2.5 to 363 nmol $\text{CH}_{4(g)}$ per gram of olivine. For comparison, recent whole rock analyses of partially serpentinized peridotite from the Mid-Cayman Rise and the Zambales ophiolite indicate minimum $\text{CH}_{4(g)}$ contents of 2 to 37 nanomoles (nmol) per gram of rock (6). If it is assumed that peridotite constitutes at least 5% of the seafloor in the Atlantic (12), Arctic, and Indian Oceans, and that 77% of the peridotite contains 75 wt. % olivine with fluid-inclusion-hosted CH_4 concentrations of 2.5 to 363 nmol $\text{CH}_{4(g)}$ per gram of olivine, we calculated that the uppermost kilometer of mantle peridotite at slow- and ultraslow-spreading ridges contains a combined mass of 2.5 to 367 Tg $\text{CH}_{4(g)}$ globally. Note that this minimum estimate does not include peridotite at passive margins, subduction zone forearcs, fast-spreading ridges, and ophiolites, which may contain additional CH_4 .

The lower oceanic crust likely represents an even larger reservoir of abiotic CH_4 than the upper mantle. Gabbro is the dominant rock type in the lower oceanic crust (12) and, as the present study demonstrates, olivine in gabbro can contain abundant $\text{CH}_{4(g)}$ -rich secondary fluid inclusions. Grozeva et al. (6) reported minimum concentrations of 72 to 310 nmol $\text{CH}_{4(g)}$ per gram of gabbro in fluid inclusions hosted in olivine, plagioclase, and clinopyroxene. If we assume that gabbro occurs in least 50% of the area in the Atlantic, Arctic, and Indian Oceans, that gabbro contains at least 72 nmol $\text{CH}_{4(g)}$ g^{-1} (6), and that the thickness of the gabbro layer at slow-spreading ridges, although highly variable, is close to 4 km on average (13, 14), the total amount of $\text{CH}_{4(g)}$ contained in the lower oceanic crust is on the order of 4.8 Pg.

Combining this value with CH_4 stored in upper-mantle peridotite suggests that the fluid-inclusion-hosted lithospheric CH_4 reservoir created at slow- and ultraslow-spreading midocean ridges exceeds the amount of preindustrial CH_4 in the atmosphere (~ 2 Pg) (15). This estimate does not include the potential contribution of CH_4 hosted in fluid inclusions in the faster-spreading Pacific lithosphere. Our analysis of 2 sites in the Pacific (Hess Deep and Cocos Plate) yield contrasting results, which precludes a meaningful assessment at this point. However, the oceanic lithosphere in the Pacific contains additional, potentially massive amounts of abiotic CH_4 that remain to be quantified when more gabbro and peridotite samples from layered oceanic crust become available.

Serpentinization and $\text{CH}_{4(g)}$ Formation within Olivine-Hosted Fluid Inclusions

Electron microscope and confocal Raman analyses indicate that iron-bearing serpentine (chrysotile, lizardite, antigorite), iron-bearing brucite, and magnetite daughter minerals line the walls and occupy the interiors of fluid inclusions while the pore space is occupied by $\text{H}_{2(g)}$ or $\text{CH}_{4(g)}$, or both (Fig. 3 and *SI Appendix*, Figs. S1–S5 and Table S2). The dominant assemblage serpentine-brucite-magnetite- $\text{H}_{2(g)}$ - $\text{CH}_{4(g)}$ provides robust evidence for serpentinization of the olivine interior under closed-system conditions (16). This assemblage is not limited to olivine-hosted fluid inclusions in ultramafic rocks, but is also common in olivine-hosted fluid inclusions in gabbroic rocks, indicating that serpentinization occurs in a wide range of protoliths. While no liquid water was detected in any of the inclusions examined, liquid water must have been present at the time of entrapment and was subsequently consumed by the formation of hydrous minerals at the expense of the olivine host. Accessory daughter minerals (typically < 5 vol. %) detected in some inclusions include calcite, dolomite, magnesite, pentlandite, awaruite, talc, sylvite, and halite (*SI Appendix*, Fig. S4). Since dissolution of olivine can only contribute Mg, Fe, Si, and minor amounts of Ni and Ca for subsequent mineral formation, the presence of these accessory minerals indicates that trapped fluids contained additional of Na, K, Cl, S, and C. Furthermore, the occurrence of talc in some inclusions points to elevated concentrations of dissolved Si in the fluid from which it precipitated. Dissolved Si was likely derived from interaction of fluids with the host rock prior to fluid inclusion formation. Although the origin of the trapped fluids cannot be unequivocally determined, the presence of Na, K, and Cl is consistent with a seawater-like source fluid. Indeed, fluid-inclusion-bearing rocks from the Mid-Cayman Rise (*SI Appendix*, Table S1) have oxygen isotope

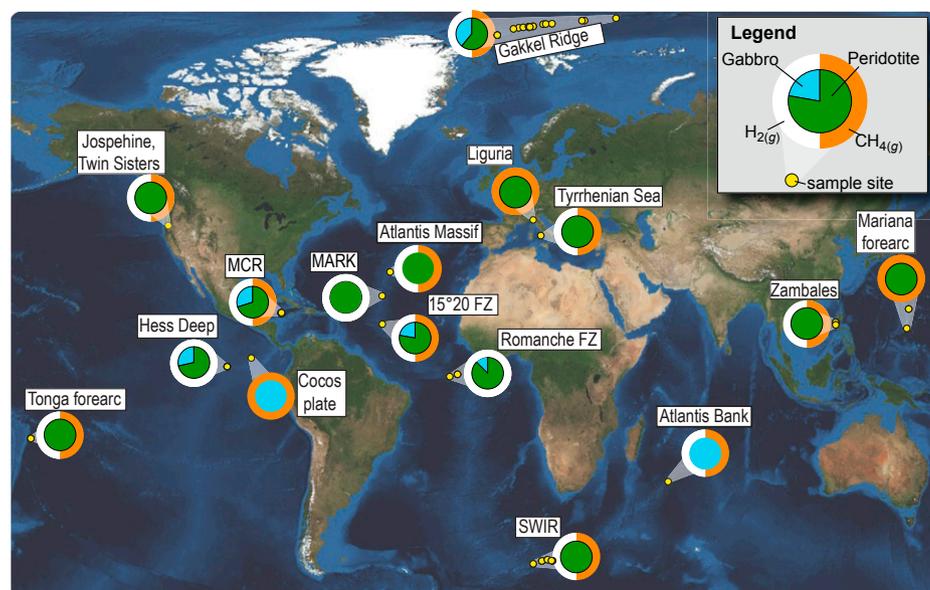
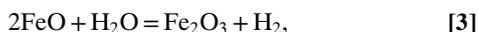


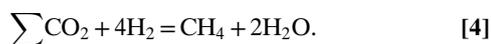
Fig. 1. Map showing the distribution, host rock type, and volatile contents of samples examined in this study. Note that inner circle of pie chart indicates proportions of olivine and gabbro whereas the color of the outer circle indicates the presence (or absence) of $\text{H}_{2(g)}$ (white) and $\text{CH}_{4(g)}$ (orange).

amount of trapped water inside an inclusion is small relative to the amount of olivine, reaction 2 can proceed until liquid water trapped in the inclusion is exhausted.

The water-driven oxidation of ferrous iron in olivine to ferric iron in magnetite and serpentine yields H₂, as represented by the generalized reaction



where FeO and Fe₂O₃ represent the ferrous iron component of olivine and the ferric iron components of magnetite and serpentine, respectively. Consequently, fluids within the inclusion interior become increasingly H₂-rich as serpentinization proceeds. The model predicts the highest H₂ yields at ~300 °C (Fig. 4A) when the amount of magnetite present in the equilibrium mineral assemblage reaches a maximum (16). Indeed, the presence of magnetite and Fe contents of serpentine and brucite (*SI Appendix, Fig. S5 and Table S2*) suggest serpentinization temperatures of 250 to 300 °C within the inclusions (16). Confocal Raman spectroscopy revealed the presence of H_{2(g)} in numerous olivine-hosted secondary fluid inclusions (Fig. 3 and *SI Appendix, Figs. S1, S2, and S4 and Table S1*), which is consistent with fluid mineral equilibria involving the mineral assemblage pentlandite-awaruite-magnetite detected in sample PS59-201-4 (27). As more H₂ is generated and water activity decreases, conditions become increasingly favorable for the reduction of $\sum\text{CO}_2$ to CH₄ (Fig. 4A) according to the reaction



Water generated by reaction 4 is available to serpentinize olivine via reactions 2 and 3, while the concurrent consumption of H₂ promotes Fe oxidation via reaction 3, thus contributing to the alteration of olivine. Together these reactions can proceed until H₂O or $\sum\text{CO}_2$ is exhausted. The equilibrium models in Fig. 4A predict an increase in CH_{4(g)} fugacity with increasing initial CO_{2(aq)} concentration at the time of entrapment. The model also suggests that CH_{4(g)} formation is thermodynamically favorable if a $\sum\text{CO}_2$ -bearing aqueous fluid trapped in olivine experiences cooling below 400 °C. Accordingly, the lack of detectable CH₄ in H₂-rich fluid inclusions from tectonic windows such as Hess Deep may reflect the absence of CO₂ in trapped fluids.

The strong temperature dependence of C speciation also implies a compositional depth stratification of olivine-hosted secondary fluid inclusions, with CO_{2(aq)} as the dominant C species in deeper zones of the oceanic crust where temperatures exceed 400 °C and CH_{4(g)} as the dominant C species in shallower zones where temperatures are lower. In ophiolites, present-day temperatures are much too low for fluid-inclusion formation to be currently ongoing at depth, suggesting that all olivine-hosted fluid inclusions formed in the geologic past either prior to obduction or during a later reheating event.

Abiotic CH₄ from Fluid Inclusions in Submarine and Subaerial Vent Systems

Recent radiocarbon and stable carbon isotope measurements, as well as mass-balance constraints of dissolved carbon species, suggest that abiotic CH₄ is not formed at the expense of $\sum\text{CO}_2$ during convection of submarine hydrothermal fluids (2–4). A magmatic source of abiotic CH₄ also seems unlikely since the upper mantle at midocean ridges is too oxidized to stabilize CH₄, and CH₄ from deeper sections in the mantle would “reequilibrate” to CO₂ and H₂O upon adiabatic decompression (28). As the present study demonstrates, olivine-hosted secondary fluid inclusions rich in CH₄ are widespread in the lower oceanic crust and upper mantle formed at midocean ridges. Leaching of olivine-hosted fluid inclusions represents a mechanism for the addition of abiotic CH₄ to circulating hydrothermal fluids in submarine serpentinization systems that is not at odds with available geological and geochemical constraints (2, 3, 6). Methane trapped in fluid

inclusions has carbon isotopic compositions consistent with those of abiotic CH₄ in submarine serpentinization systems (6). Because CH₄ is formed in isolation from circulating vent fluids, the carbon required for CH₄ formation is not derived from circulating fluids, in keeping with measured vent fluid compositions (3). Moreover, CH₄ may be trapped within fluid inclusions for geologically significant periods of time resulting in a radiocarbon-poor CH₄ reservoir within the oceanic crust. Leaching of this CH₄ would account for the occurrence of radiocarbon-poor abiotic CH₄ in submarine hydrothermal fluids associated with serpentinization (3, 4). Together, these observations support the idea that olivine-hosted fluid inclusions represent a potentially significant source of abiotic CH₄ in submarine hydrothermal systems influenced by serpentinization.

Fluid inclusions in submarine serpentinization systems may also represent a source of abiotic CH₄ in mafic-hosted submarine hydrothermal systems that access gabbroic rocks. Fluids venting from mafic-hosted hydrothermal systems are typically characterized by much lower CH₄ concentrations than fluids venting from serpentinite-hosted hydrothermal systems. The large difference in concentrations notwithstanding, fluids from both environments show remarkably similar carbon isotopic compositions (2–4, 29, 30). The isotopic similarity points to a common underlying process responsible for CH₄ formation in these diverse substrates (2, 3). In this respect, it is important to note that serpentinization within olivine-hosted fluid inclusions in gabbro creates conditions conducive to CH₄ formation that are independent of the redox conditions in the surrounding rock and percolating fluids. Deeply penetrating hydrothermal fluids interacting with fluid-inclusion-bearing gabbro would have the same compositional features as fluids interacting with basalt, but be enriched in CH₄. Indeed, fluids venting from the mafic-hosted Menez Gwen hydrothermal system exhibit CH_{4(aq)} concentrations of up to 2.15 mmol/kg despite having many compositional features typical of mafic-hosted systems such as relatively high SiO_{2(aq)} and low H_{2(aq)} concentrations (30). Methane in fluids venting from mafic-hosted hydrothermal systems that have similar carbon isotopic compositions, but lower concentrations (29), may reflect more limited access to gabbroic rocks in the underlying plumbing systems. The emerging picture suggests that fluid inclusions represent a significant source of abiotic CH₄ in both mafic-hosted and ultramafic-hosted submarine hydrothermal systems.

Olivine-hosted secondary fluid inclusions were found in all continental field locations indicated in Fig. 1. From these field areas, active venting of CH₄ has been documented at Zambales (1) and in the Ligurian Alps (31). As is the case for submarine hydrothermal systems, derivation of abiotic CH₄ by leaching from fluid inclusions is consistent with available constraints in continental serpentinization sites. Helium isotopes and stable carbon isotopic compositions of CH₄ in fluid inclusions overlap with those measured at continental CH₄ seeps (1, 6). Moreover, fluid inclusions were formed in the distant geological past (>50 ka) and therefore CH₄ is likely radiocarbon-free, as is observed in CH₄ from continental seeps (1). Olivine-hosted fluid inclusions from continental peridotites examined in this study show a range of CH₄ pressures with some of the highest (55 MPa) in the entire sample collection (*SI Appendix, Table S1*). Based on the results of this study, we can assess whether abiotic CH₄ trapped in fluid inclusions can account for the quantities of CH₄ released from continental seeps. For instance, the Chimaera serpentinization system in Turkey has released 0.076 to 0.5 km³ CH₄ during the past 2 millennia (32, 33). If a source rock volume of 12 km³ (32) is assumed, and that peridotite at Chimaera contains 75 wt. % olivine, the CH₄ abundances of 2.5 to 363 nmol CH_{4(g)} per gram of olivine in peridotite would yield 0.002 to 0.26 km³ of fluid-inclusion-derived CH₄, broadly consistent with the amounts of CH₄ released at Chimaera (*SI Appendix, Fig. S7*).

An alternative model involving CO₂ reduction via Sabatier reactions in gas-filled fractures, with requisite radiocarbon-free CO₂ derived from nearby sediments, has been proposed by Etiope and Whiticar (33) for the origin of abiotic CH₄ in continental serpentinization systems such as Chimaera and Zambales

represent one of the largest sources of abiotic CH₄ on Earth. Circulation of aqueous fluids in olivine-rich substrates is critical in the formation of fluid inclusions, in the release of CH₄ from fluid inclusions, and in the transport of CH₄ to vent sites where it is available to participate in numerous biogeochemical processes. Similar processes involving fluid inclusions may occur elsewhere in the solar system, with important implications for the distribution and maintenance of microbial life beyond Earth.

Methods

Thin sections were examined for fluid inclusions using a petrographic microscope. Reflected light microscopy was used to locate and examine opened inclusions. Fluid-inclusion abundances were estimated by analyzing back-scattered electron images of inclusions exposed by polishing. The mineral and volatile contents of secondary fluid inclusions were studied with a Horiba LabRam HR800 confocal Raman microscope equipped with 3 lasers (473, 532, and 633 nm), a motorized x-y-z stage, 2 gratings (600 and 1,800 grooves per millimeter), and a thermoelectric-cooled charge-coupled detector (1,024 × 256 pixels). The system was calibrated daily using a silicon wafer and a monochromatic neon light source (Oriel model 6032). We chose a 473-nm laser and a 100× objective (numerical aperture = 0.9) to resolve objects smaller than 0.6 μm. To achieve the highest possible spectral resolution for CH₄ pressure calculations using Raman band position measurements (11), we chose a 633-nm laser, a grating with 1,800 grooves per millimeter, and a slit size of 30 μm. Acquisition times ranged from 5 to 60 s per analysis. To improve signal-to-noise ratios, 3 to 5 acquisitions were averaged. Spectra were processed with the LabSpec 6 software for background correction using polynomial functions and for peak fitting using a pseudo-Voigt function. In addition to spot analysis, we acquired hyperspectral Raman maps using a 473-nm laser, 600 grooves per millimeter grating, 100 to 300 μm confocal hole diameter, 1 to 30 s acquisition time, 1 to 3 accumulation(s) per spot, and x-y step sizes of 0.5 to 2 μm. Hyperspectral Raman maps were further processed with the multivariate data analysis module integrated in the LabSpec

6 software. Measured and calculated end-member spectra were compared with reference spectra (11, 39–41).

Field-emission scanning electron microscopy (Marine Biological Laboratory) and electron microprobe analysis (FE-EMPA, Yale University) were used to examine open fluid inclusions that were exposed by careful polishing. FE-EMPA was carried out using an accelerating voltage of 15 kV and a beam current of 10 nA. Spot sizes for quantitative analyses of hydrous minerals were at least 3.5 μm to minimize beam damage. The beam was fully focused for magnetite, sulfide, and alloy measurements. Natural and synthetic standards were used for element calibration, and raw data were corrected using the Phi-Rho-Z method (42).

Fluid-inclusion analyses were complemented with thermodynamic equilibrium models for reactions between trapped aqueous fluids and the olivine host as a function of temperature and CO₂ concentration using the software code EQ3/6 (25). We used a customized thermodynamic database (16), which includes equilibrium constants calculated with the software code SUPCRT92 (43) for a temperature range of 25 to 600 °C at a constant pressure of 100 MPa. Olivine (Mg_{1.8}Fe_{0.2}SiO₄) was used as the solid starting material in all models. The salinity of the aqueous fluid was adjusted to 3.5‰, which allowed computation of equilibrium models with ionic strengths of <0.04 and water activities close to unity at water-to-olivine mass ratios of 0.2. The low water-to-olivine ratio was chosen to model reactions involving a small amount of fluid trapped in a large amount of olivine.

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