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Reaction path model of the formation of abiotic immiscible hydrocarbon fluids in subducted carbonated serpentinites, Lanzo Massif (Western Italian Alps)

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Abstract

Fluids generated from subducted slabs participate in the cycling of deep carbon in the crust and upper mantle. In these fluids, aqueous carbon species vary in oxidation state between +IV and -IV depending on whether the fluids are oxidizing or reducing, respectively. Most studies of subduction-zone fluids have focused on oxidized carbon species. However, recent studies of natural samples have demonstrated the occurrence of deep, reducing fluids, generated in both subducted oceanic upper mantle and crustal rocks. CH_4 - H_2 -rich fluid inclusions in subducted carbonated serpentinites have demonstrated the existence of abiotic, immiscible, hydrocarbon fluids at upper mantle conditions. To investigate the formation of such immiscible hydrocarbon fluids during the evolution of subducted carbonated serpentinites, we used equilibrium constants from the Deep Earth Water model to carry out predictive chemical mass transfer modeling to simulate the alteration reactions. A novel feature of the models was the inclusion of an immiscible hydrocarbon fluid containing six components ($CH_{4,f}$, $C_2H_{6,f}$, $C_3H_{8,f}$, $isoC_4H_{10,f}$, $CO_{2,f}$, $H_{2,f}$). This feature enabled prediction of the formation of a separate immiscible fluid in equilibrium with aqueous species and minerals.

We developed a predictive reaction path model of invasive $H_{2,f}$ reacting with carbonated serpentinites and interstitial aqueous fluids for comparison with the natural samples from the Lanzo Massif, western Italian Alps. Over a range of temperatures and pressures, immiscible hydrocarbon fluids formed in association with altered mineral assemblages. Reaction progress caused the transformation of carbonated serpentinites and the formation of clinopyroxene, brucite, graphite, and hydrocarbon fluids, along with changes of pH , $\log f_{O_2}$, and aqueous species. $CH_{4,f}$ was the most abundant hydrocarbon species in all the models. The overall results at 2.0 GPa and

400 to 450 °C were consistent with the natural samples from the Lanzo Massif. Interestingly, large amounts of H_2O formed due to oxidation of H_2 . More hydrocarbons and H_2O formed in models with lower fluid/rock mass ratios or with more reactant H_2 . Models at different pressure and temperature conditions showed similar results with some variation in the relative stabilities of aragonite, graphite and olivine solid solution, and associated differences in mineral sequences, hydrocarbon fluids, values of aqueous species, and the final $\log f_{O_2}$ and pH . Our models strongly support the laboratory and field evidence that reduction of carbonated serpentinites by infiltrating H_2 fluids can cause the formation of immiscible, abiotic hydrocarbon fluids in subduction zones.

Key words:

Abiotic hydrocarbon; Carbonated serpentinites; DEW model; Thermodynamic modeling; Deep carbon fluids

Highlights

- Novel reaction path model for invasive H₂ fluids interacting with carbonated serpentinites
- Use of the Deep Earth Water model for predictive chemical mass transfer modeling
- Significant immiscible CH₄ fluid and H₂O formed under high pressure and temperature
- Serpentinite and aragonite destroyed with brucite, graphite, and clinopyroxene formed
- Model results agree with natural samples from Lanzo Massif, western Italian Alps

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1 **1. Introduction**

2 It has long been proposed that hydrocarbon fluids could exist in the deep Earth (Mendeleev
3 1877, Kudryavtsev 1959, Kolesnikov *et al.* 2009, 2017, Kutcherov and Krayushkin 2010).
4 Although controversial (McCollom 2013, Sephton and Hazen 2013), a deep, abiotic theory for the
5 origin of hydrocarbons received support in the late 20th century from the hypothesis of a deep hot
6 biosphere feed by ascending abiotic fluid hydrocarbons from the deep Earth (Kudryavtsev 1951,
7 Gold 1992, 2001). However, the amounts of abiotic hydrocarbons that could be produced in the
8 upper mantle were never quantified and remain highly speculative.

9 Recent studies have suggested evidence of possible abiotic hydrocarbon- H_2 -bearing fluids
10 in association with ultramafic or mafic rocks and serpentinization in mid-ocean ridge settings
11 where the hydrocarbons are present in minor quantities dissolved in the circulating aqueous fluids
12 (Proskurowski *et al.* 2008, Alt *et al.* 2013, McDermott *et al.* 2015, Klein *et al.* 2019). However, it
13 is doubtful that the CH_4 formed recently in the present hydrothermal circulation systems
14 (McDermott *et al.* 2015, Reeves and Fiebig 2020). For example, Klein *et al.* (2019) suggested that
15 H_2 and CH_4 can be formed inside olivine-hosted aqueous fluids as a result of host-inclusion
16 interactions during cooling and subsequently released into the mid-ocean ridge hydrothermal
17 circulation system.

18 Many fewer studies have been concerned with hydrocarbon production during high-
19 pressure metamorphism in subduction zones, where most studies have typically focused on
20 oxidized carbon species dissolved in the fluid phases (Hacker *et al.* 2003, Dasgupta and
21 Hirschmann 2010, Scambelluri *et al.* 2019). Subduction zone serpentinization has been proposed
22 to produce large amounts of H_2 and CH_4 (Vitale Brovarone *et al.* 2020). Additionally, CH_4 has

23 been found in high-pressure and ultra-high-pressure metabasic rocks (Tao *et al.* 2018, Zhu *et al.*
24 2020). Experimental and theoretical studies have demonstrated that H_2 and light hydrocarbons can
25 be immiscible at subduction zone conditions (Huang *et al.*, 2017; Huang *et al.*, 2023; Li, 2017;
26 Pruteanu *et al.*, 2017). However, the generation of reduced-carbon species in subduction zone
27 fluids or as immiscible phases has not received much attention. Nevertheless, natural confirmation
28 of immiscible, CH_4 - H_2 -bearing fluids related to serpentinization in subduction zones have now
29 been found world-wide. For example, coexisting aqueous and H_2 - CH_4 -rich gaseous fluid
30 inclusions in the Lanzo massif, western Italian Alps (Pelletier and Müntener 2006, Vitale
31 Brovarone *et al.* 2017, 2020, Giuntoli *et al.* 2020, Sverjensky *et al.* 2020) have been suggested to
32 document immiscibility of reduced fluids in metamorphic fluids. In these rocks, CH_4 formed by
33 H_2 -mediated reduction of carbonate in carbonated serpentinites. The reaction also resulted in the
34 formation of diopside, brucite, graphite, \pm Ca-rich garnet (Vitale Brovarone *et al.* 2017, Giuntoli *et*
35 *al.* 2020). A recent geochronological study indicates that the event of CH_4 formation happened at
36 peak metamorphic conditions (Piccoli *et al.* 2023), corresponding to about 500 °C and depths up
37 to 80 km, or \sim 2.5 GPa (Vitale Brovarone *et al.*, 2017 and references therein).

38 In addition to natural examples of abiotic hydrocarbons, numerous experimental studies of
39 abiotic hydrocarbon formation at elevated temperatures and pressures have been reported
40 (Foustoukos and Stern 2012, Manning *et al.* 2013, McCollom 2013). Under crustal conditions, the
41 formation of hydrocarbons in serpentinization experiments has been widely studied with and
42 without catalysts such as metallic iron (Barbier *et al.* 2020). At higher, upper mantle pressures,
43 experimental studies have focused on fluids without minerals present. For example, immiscible
44 CH_4 - C_2H_6 - H_2 fluid inclusions were recorded in quartz at 1.5 - 2.5 GPa and 600 - 700 °C (Li 2017),
45 and immiscible hydrocarbon droplets containing isobutane and other hydrocarbons were observed

46 with *in situ* Raman spectroscopy at 1.6 – 4.6 GPa and 300° C (Huang et al., 2017; Huang et al.,
47 2023).

48 Overall, natural examples and experiments at upper mantle temperatures and pressures
49 indicate that the formation of immiscible abiotic hydrocarbons does occur. However, quantitative,
50 predictive models of the formation of immiscible abiotic hydrocarbon fluids in geologic settings
51 at depth have been lacking. In this study, we conducted predictive, irreversible chemical mass
52 transfer modeling to simulate the formation of hydrocarbon fluids in a well-documented natural
53 setting. We chose to model the reduction of carbonated serpentinites and the associated production
54 of an immiscible CH_4 -rich fluid in the Lanzo Massif previously described in detail by Vitale
55 Brovarone et al. (2017). Following the genetic model by Vitale Brovarone et al. (2017), we
56 modeled the interaction between H_2 -rich fluids and carbonated serpentinites in the pressure and
57 temperature range of 1.0 - 2.0 GPa and 400 - 500 °C which is consistent with reported subduction
58 zone conditions (Van Keken *et al.* 2002, Syracuse *et al.* 2010, Penniston-Dorland *et al.* 2015, Holt
59 and Condit 2021). Our models provide a test of our ability to predict the formation of immiscible
60 hydrocarbon fluids in a chemically and mineralogically complex system at elevated pressure-
61 temperature conditions for comparison with the observed mineral assemblages and fluid inclusion
62 compositions previously described for the reduced carbonated serpentinites from the Lanzo Massif.

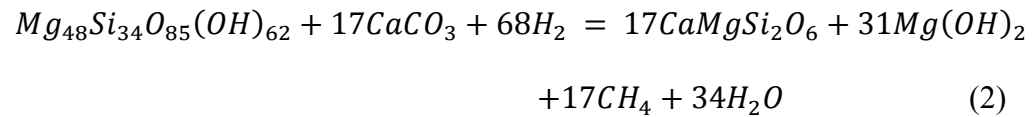
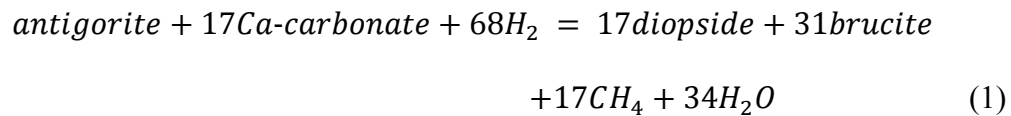
63 **2. Geologic setting of the Lanzo Massif and abiotic methanogenesis during the** 64 **reduction of carbonated serpentinites**

65 The ultramafic rocks of the Lanzo Massif in the western Italian Alps underwent Cenozoic
66 eclogite-facies peak metamorphic conditions to about 500-550 °C and 2 GPa (Rubatto and
67 Hermann 2001, Pelletier and Müntener 2006). The massif includes carbonated serpentinites,

68 including carbonated serpentinites, regarded as the products of sub-seafloor hydrothermal
69 reactions (Lagabrielle *et al.* 1990, Rubatto and Hermann 2001, Pelletier and Müntener 2006, Vitale
70 Brovarone *et al.* 2017). The carbonated serpentinites are located in the pervasive serpentinized
71 shell outside the peridotite core of the massif. The shell surrounds mostly the north and west sides
72 of the peridotite core. For the purposes of the present study, the detailed petrographic, fluid
73 inclusion, isotopic, modeling, and geochronological results reported by Vitale Brovarone *et al.*
74 (2017), Giuntoli *et al.* (2020), and Piccoli *et al.* (2023) can be summarized by the following key
75 points relevant to our reaction path modeling:

- 76 • The samples of carbonated serpentinite consist of clasts of serpentinite embedded in a Ca-
77 carbonate matrix.
- 78 • Pristine serpentinite clasts consist mainly of antigorite – the serpentine mineral stable at
79 high temperature and pressure conditions – and small amounts of chlorite and magnetite.
- 80 • The reacted serpentinite clasts are coated by ubiquitous graphite rims. Other product
81 minerals include diopside ± brucite ± Ca-rich garnet ± perovskite (CaTiO₃).
- 82 • The reacted rocks are found along discrete layers within the carbonated serpentinite, which
83 were interpreted as fluid pathways and shear zones (Giuntoli *et al.* 2020). Overall, the
84 degree of alteration of the serpentinite clasts is highly variable on a spatial scale of meters.
- 85 • Petrographic relations indicate that graphite formation occurred at high-pressure conditions
86 in the antigorite stability field. Dating of syn-reduction perovskite including CH₄ and
87 graphite inclusions provided an age of 49.6 ± 1 Ma (Piccoli *et al.* 2023), which is consistent
88 with previous constraints on the peak metamorphic age of the Lanzo massif (Rubatto and
89 Hermann, 2001).

- 90 • Two types of structurally coexisting fluid inclusion populations were found in the
 91 carbonate matrix adjacent to serpentinite clasts and the reacted rims of serpentinite: a CH_4 -
 92 H_2 -rich population and a H_2O -rich population. These two populations were interpreted to
 93 represent coexisting immiscible fluids (Vitale Brovarone *et al.* 2017, Sverjensky *et al.*
 94 2020).
- 95 • The $\delta^{13}C$ values of the residual, reacted carbonate samples are up to about 8 per mil
 96 heavier than the least reacted samples which have typical marine carbonate values of about
 97 2 - 3 per mil relative to the PeeDee Belemnite standard (Vitale Brovarone *et al.* 2017).
 98 These values are consistent with the partial transformation of carbonate into CH_4 .
- 99 • The CH_4 genesis was interpreted as the result of H_2 -carbonate interactions along
 100 channelized fluid pathways inside the carbonated serpentinite. The process was
 101 summarized according to the following overall reaction:



- 106 • Overall, the mineral assemblages and fluid inclusions suggest the reduction of carbon in
 107 Ca-carbonate by the H_2 -fluids to form CH_4 and graphite. Reaction between the external H_2
 108 and the newly formed graphite was also proposed to generate additional CH_4 .
- 109 • The pressure and temperature conditions of the reactions were determined by the presence
 110 of graphite and aragonite inclusions in magnetite, and syn-reduction antigorite, and
 111 modeled in a simplified *Ca-Mg-Si-C-O-H* thermodynamic system. The minimum
 112 condition was inferred to be 1.0 GPa and 370 °C (i.e., 370 °C GPa^{-1} of gradient, same as

113 below) constrained by graphite-aragonite coexistence along the exhumation path of the
114 Lanzo massif. The maximum condition was predicted to be about 2.5 GPa and 500 °C (200
115 °C GPa^{-1}) constrained by the peak metamorphic condition of the Lanzo Massif.

- 116 • The oxygen fugacities during the reactions were estimated to range from $\log f_{O_2}$ -29 to -37
117 (QFM -3 to -6), assuming graphite saturation and the co-occurrence of magnetite in the
118 carbonated serpentinites.

119 **3. Methods**

120 ***3.1 Thermodynamic data for aqueous species and minerals***

121 We have used the geochemical Deep Earth Water (DEW) model which was built to address
122 the predictive geochemical modeling challenge of a huge range of temperatures, pressures, and
123 chemically complex systems (Sverjensky *et al.* 2014, Huang and Sverjensky 2019,
124 Sverjensky 2019). The DEW model is based on predictive geochemical theory resting on
125 decades of theoretical and experimental studies of the thermodynamic properties of electrolytes,
126 neutral aqueous solutes, metal-complexes, and organic species. The DEW model enables
127 prediction of equilibrium constants involving aqueous species of all types to be incorporated into
128 the data files for aqueous speciation, solubility, and chemical mass transfer codes. Here we use the
129 codes EQ3 & EQ6 (Wolery 1992) modified to operate at elevated temperatures and pressures. The
130 standard Gibbs free energies of formation of the end-member mineral components were calculated
131 with the modified Berman thermodynamic database (Berman 1988, Sverjensky *et al.* 1991,
132 Sverjensky 2019).

133

134

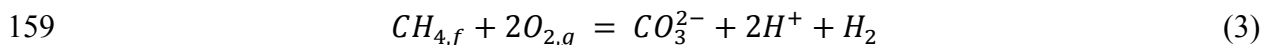
135 **3.2 Standard Gibbs free energies of fluid H₂ and CO₂**

136 The calculation of chemical mass transfer involving immiscible hydrocarbon fluids
137 requires the computation of standard Gibbs free energies of the pure end-member hydrocarbon
138 species as well as other pure fluid species that are relevant to the modeling described below. Here
139 we made use of six organic and inorganic pure fluid species, all of which are relevant to this study.
140 These fluid species include the following: methane ($CH_{4,f}$), ethane ($C_2H_{6,f}$), propane ($C_3H_{8,f}$),
141 isobutane ($isoC_4H_{10,f}$), carbon dioxide ($CO_{2,f}$), and hydrogen ($H_{2,f}$) where the subscript f refers
142 to the supercritical fluid compound. The apparent standard Gibbs free energies of formation
143 ($\Delta G_{f;T,P}^0$) of these species are given in the Appendix A. They were obtained by first calculating the
144 $\Delta G_{f;T,P^0}^0$ of the pure gas, then the fugacity coefficients (ϕ) were obtained from the GFluids
145 spreadsheet (Zhang and Duan 2010) at 1.0 - 5.0 GPa and 300 - 650 °C (values below 400 °C were
146 extrapolated to 300 °C using the data from the higher temperatures). Equilibrium constants
147 involving these species and aqueous species were calculated using the DEW model and
148 incorporated into the data files for the codes EQ3 and EQ6.

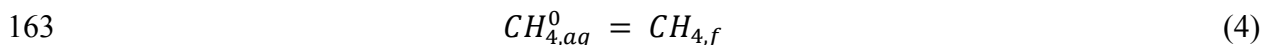
149 **3.3 Incorporation of hydrocarbon fluids in aqueous speciation, solubility, and chemical mass** 150 **transfer models**

151 Although aqueous C-species of many types in the spectrum of inorganic to organic species
152 have long been used in aqueous speciation, solubility, and chemical mass transfer models,
153 immiscible inorganic or organic fluids have not been used in such models. Here, we incorporated
154 such species using a number of approximations. Mathematically, this incorporation can be done
155 by including the predicted $\log K$ values for equilibrium between any potentially immiscible fluid

156 species (e.g. $H_{2,f}$ or $CH_{4,f}$) and a strict basis species into the thermodynamic data file as a "mineral
157 species". For example, we decided to put fluid methane ($CH_{4,f}$) into the datafile of EQ3 and EQ6
158 using the equilibrium



160 During model calculations, the above equilibrium enables the fluid species to reach
161 saturation and "precipitate" as a pure fluid phase immiscible with the aqueous fluid and any
162 minerals in equilibrium with the aqueous fluid according to the reaction



164 Examples of reactions such as Eq. (4), which are just solubility reactions, are discussed below as
165 functions of temperature and pressure.

166 Building on the above, two or more such potentially immiscible fluid species can be entered
167 as potential components of a "solid-solution" in the data file of the codes EQ3 and EQ6, which
168 enables formation of an immiscible fluid phase (e.g., a hydrocarbon fluid phase containing
169 multiple hydrocarbon components). In the present study, the end-member components of the
170 immiscible hydrocarbon fluid were assumed to mix ideally. At elevated temperatures and pressures,
171 this is a major assumption. However, in almost all our model results the hydrocarbon fluid that
172 formed was greater than 90% fluid CH_4 . Therefore, as a first approximation, it seems reasonable
173 to assume ideal mixing in the hydrocarbon fluid.

174 ***3.4 Conceptual model and assumptions for chemical mass transfer calculations***

175 As discussed above, the carbonated serpentinite of interest consisted of clasts of
176 serpentinite embedded in an aragonite matrix. The serpentinite is composed mainly of antigorite
177 with minor magnetite and chlorite. We assume here a conceptual model in which an external H_2
178 fluid invades and reacts with the carbonated serpentinite assemblages that contain some interstitial

179 aqueous fluid. As a first approximation, the composition of this initial interstitial fluid was
180 assumed to be determined by equilibrium with the rock minerals. Using the aqueous speciation
181 and solubility code EQ3 (Wolery 1992), the concentrations of the elements Ca, Si, Fe, and Al,
182 were determined by equilibrium with aragonite, antigorite, magnetite, and the clinocllore
183 component of a chlorite solid solution (X_{Mg} 0.97), respectively. Mg was set to a value below the
184 saturation of brucite. Na and Cl were set to low values of 0.001 m as the salinity of the aqueous
185 fluid predating the reactions is not known. C was set to a small value, e.g. ≤ 0.1 molal, in
186 equilibrium with aragonite, so the amount of aqueous C is not important in the initial fluid. Either
187 Na^+ or H^+ was determined by charge balance leading to a calculated value of the pH . Wide
188 ranges of the initial value of the $\log f_{O_2}$ were tested. Optimal values were selected based on the
189 constraints of minimizing the initial aqueous carbon concentration in equilibrium with aragonite
190 such that the computed aqueous Ca concentrations were not so high as to result in supersaturation
191 of the initial fluid with respect to diopside or clinopyroxene solid solution. These constraints
192 typically resulted in $\log f_{O_2}$ values of QFM to QFM - 2. As an example, the bulk composition and
193 most abundant C-species and fluid properties of an initial fluid at 400°C and 2.0 GPa are listed in
194 Table 1 where it can be seen that the $\log f_{O_2}$ is equal to QFM-1.3.

195 The initial aqueous fluids were subsequently used as input to the chemical mass transfer
196 code (EQ6), together with the carbonated serpentinite reactant minerals and external H_2 fluid
197 reactant. The Lanzo carbonated serpentinite was approximated by 15 vol% of aragonite and 85
198 vol% of serpentinite. The serpentinite contained 96.5 vol% of antigorite, 1.0 vol% of magnetite,
199 and 2.5 vol% of chlorite. This assumption of a standard run provides an example of the
200 composition of the carbonated serpentinites. Additional models were considered for higher
201 aragonite/serpentinite ratios (Appendix A). To explore the effect of variable fluid-rock (F/R) ratio,

202 the total amount of reactant rocks was varied from 669 g to 10,000 g per 1,000 g of H_2O in the
203 initial aqueous fluid. The initial amount of reactant H_2 in moles per 1,000 g of H_2O was
204 determined by the need to overwhelm the redox buffering capacity of the initial rock in order to
205 form hydrocarbon fluid. Within the framework of the assumptions adopted above, numerous
206 reaction path models were run to explore variable temperatures, pressures, initial oxidation states,
207 and F/R ratios. A representative set of these is included in the Supplementary Materials. The
208 overall goal was to compare the predicted model outputs to the mineral assemblages in the rocks
209 and the hydrocarbon fluids recorded in fluid inclusions reported for the Lanzo Massif by Vitale
210 Brovarone et al. (2017) and Giuntoli et al. (2020).

211 **4. Results**

212 ***4.1 Predicted equilibria between fluid hydrocarbons, aqueous C-species, and graphite at upper*** 213 ***mantle conditions***

214 ***4.1.1 Predicted equilibria between pure immiscible fluids and aqueous species***

215 Either H_2O -bearing and CH_4 - H_2 fluids were observed in microstructurally coexisting fluid
216 inclusions populations of the Lanzo reduced carbonated serpentinite, suggesting at least two types
217 of immiscible fluids could appear in the natural samples. Accordingly, a number of fluid phases,
218 including hydrocarbon and inorganic species at upper mantle conditions were incorporated in our
219 model. The values of the equilibrium constants were predicted using the DEW model (Sverjensky
220 et al. 2014) adapted for equilibria between pure fluid and aqueous species. The standard states for
221 the fluid species $CH_{4,f}$, $C_2H_{6,f}$, $CO_{2,f}$, and $H_{2,f}$ were chosen to be the pure fluids at the
222 temperatures and pressures of interest. Equilibria between such fluids and the corresponding

223 aqueous species represent the maximum activities of the aqueous species, i.e. the solubility of the
224 pure fluid component as an aqueous species.

225 The predicted $\log K$ values displayed in Figs. 1A - D cover a wide range of temperatures
226 and pressures from 300 - 650 °C and 0.5 - 5.0 GPa. It can be seen in the figures that, overall, the
227 $\log K$ values increased with temperature and decreased with pressure, with some exceptions at 0.5
228 - 1.0 GPa. In another words, the solubilities of fluid $CH_{4,f}$, $C_2H_{6,f}$, $CO_{2,f}$, and $H_{2,f}$ in aqueous
229 solutions increase with temperature but decrease with pressures greater than about 1.5 GPa. At
230 temperatures between 400 and 500 °C, the solubilities decrease in the order: $CH_4 < C_2H_6 < H_2 <$
231 CO_2 . As a first order generalization, it should therefore be easier to form immiscible CH_4 -rich
232 fluids than any of the others.

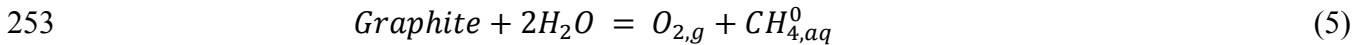
233 Although the equilibria shown in Figs. 1A-D are fundamental to the formation of
234 immiscible fluids, other factors also may exert a strong influence. Clearly, the redox state of a
235 system is extremely important. For example, if the $\log f_{O_2}$ is low enough, the formation of a CH_4
236 -rich fluid will be strongly favoured relative to the other C-species. This tendency can be expected
237 to be magnified when the H_2 is continuously added and reacted with minerals. Furthermore, the
238 equilibria between aqueous and fluid species depends on $\log f_{O_2}$, pH , total C content and other
239 features of the system. Different results could occur with a wider range of conditions beyond the
240 scope of this work.

241 4.1.2 Predicted equilibria between pure fluid methane, aqueous methane, and graphite

242 Graphite was an important product in the Lanzo reduced carbonated serpentinite and was
243 observed to be closely related to the CH_4 - H_2 fluid inclusions (Vitale Brovarone *et al.* 2017). In
244 Fig. 2, the stability fields of aqueous CH_4 , pure fluid CH_4 ($CH_{4,f}$) and graphite were plotted as

245 functions of $\log f_{O_2}$ and $\log a_{CH_4, aq}^0$ at 1.0 - 2.0 GPa and 400 - 500 °C (Fig. 2). The equilibrium
 246 between aqueous and fluid CH_4 is determined solely by the equilibrium in Fig. 1A. It can be seen
 247 that the predicted $\log a_{CH_4, aq}^0$ in equilibrium with $CH_{4, f}$ range from 0.4 to 1.1 in Figs. 2A -D. The
 248 activity coefficient of $\log a_{CH_4, aq}^0$ was assumed to be unity in our subsequent modeling. As
 249 expected from Fig. 1A, the stability field of $CH_{4, f}$ expanded against $CH_{4, aq}^0$ at lower temperature
 250 and higher pressure.

251 The equilibrium between fluid $CH_{4, f}$ and graphite can be expressed in terms of $\log f_{O_2}$ by
 252 writing the reaction



254 From which the $\log f_{O_2}$ can be expressed by the $\log K$ of Eq. (5) and $\log a_{CH_4, aq}^0$ as

$$255 \quad \log f_{O_2} = -\log a_{CH_4, aq}^0 + \log K \quad (6)$$

256 assuming that a_{H_2O} is unity. In Figs. 2A - D, this equilibrium is expressed as a line with a slope
 257 of -1.0 and intersecting the line representing equilibrium between $CH_{4, f}$ and $CH_{4, aq}^0$ at an
 258 invariant point. It can also be seen that the equilibrium between fluid CH_4 and graphite is about
 259 3.0 log units below the QFM buffer, in agreement with the prediction by Vitale Brovarone et al.
 260 (2017). We also included the magnetite- α -Fe buffer, and the H_2O - $H_{2, f}$ buffers with $a_{H_2, f}$ of 0.1
 261 and 1.0. These buffers all plot in the $CH_{4, aq}$ and $CH_{4, f}$ fields.

262 The phase diagrams in Figs. 2A - D provided guidance for setting up the initial $\log f_{O_2}$ of
 263 our model aqueous fluid resulting in values above the $CH_{4, aq}^0$ field and amounts of initial carbon
 264 lower than saturation with graphite or $CH_{4, f}$. Starting from these conditions, when $\log f_{O_2}$
 265 decreases, and when $CH_{4, aq}^0$ increases, the figures show that it can be expected that the boundary

266 of $CH_{4,aq}^0$ and $CH_{4,f}$ will be reached, followed by the stability field of CH_4 -rich hydrocarbon
267 fluid.

268 It should be noted here that although graphite appears as a phase in Figs. 2A - D, these
269 figures refer to a chemical system without the component CaO , an important component in the
270 natural carbonated serpentinites. When CaO is included, the stability of graphite is limited by the
271 appearance of aragonite or calcite solid solution, depending on the value of the
272 $\log \left(\frac{a_{Ca^{2+}}}{(a_{H^+})^2} \right)$ in the aqueous phase. For the conditions we modeled below, the stability field
273 of graphite is replaced by aragonite or calcite solid solution at 1.0 GPa and 400°C.

274

275 ***4.2 Fluid hydrocarbon formation during the destruction of carbonated serpentinites in the*** 276 ***Lanzo Massif***

277 Chemical mass transfer models of the transformation of carbonated serpentinites by H_2
278 fluids were conducted at 1.0 - 2.0 GPa and 400 °C - 500 °C consistent with the conditions proposed
279 for the Lanzo Massif (Vitale Brovarone *et al.* 2017). The initial aqueous fluids were predicted at
280 each pressure and temperature condition (Table 1, S-1, S-2, S-3, S-4) using an aqueous speciation
281 solubility model as described above (section 3.3). The initial total concentrations of the aqueous
282 carbon were 0.01, 0.05, or 0.1 molal, which were the lowest values usable given our assumptions
283 about equilibrium with the minerals and with initial $\log f_{O_2}$ values between QFM -1.6 to +1.2. The
284 saturation activity of $CH_{4,aq}^0$ increased with temperature at the same pressure. The carbon
285 speciation in the initial fluids was controlled by $\log f_{O_2}$ relative to the QFM buffer and the total
286 aqueous carbon concentrations. For example, at 1.5 GPa and 400 °C, two oxidation states could
287 be considered: at $\log f_{O_2}$ of QFM+1.0, $CH_{4,aq}$ is 0.03% of the total carbon of 0.01 m, whereas at

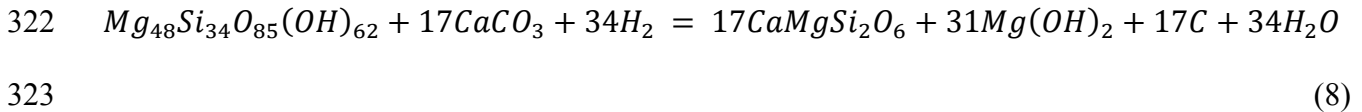
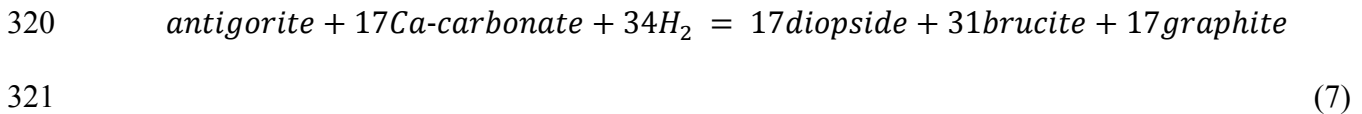
288 $\log f_{O_2}$ of QFM-1.4, $CH_{4,aq}$ is 91.4% of the total carbon of 0.1 m. Importantly, the different
289 oxidation states of these two fluids did not affect the major results of the mass transfer reactions.
290 Therefore, either fluid could be used at each pressure and temperature. In other words, the initial
291 values of $\log f_{O_2}$ in the fluid were not important variables. The main reason being that in all cases
292 the total initial carbon in the fluid was low.

293 *4.2.1 The standard model at 2.0 GPa and 400.0 °C and F/R equal to 0.1*

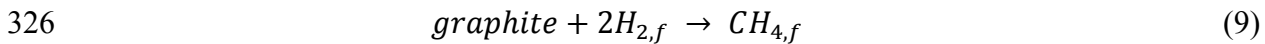
294 Here we present a mass transfer model at 2.0 GPa and 400 °C and F/R equal to 1.0 that
295 can serve as a representative example of our modeling (Table 1, Fig. 3). At this temperature and
296 pressure, the activity of $CH_{4,aq}^0$ in equilibrium with pure methane fluid was 2.4 (see Fig. 1A).
297 Therefore, as the aqueous activity coefficient in our model for neutral species was assumed to be
298 unity, at least 2.4 m $CH_{4,aq}^0$ would need to accumulate in the fluid during the mass transfer
299 reactions for an immiscible pure methane fluid to form. In our models, a hydrocarbon fluid with
300 variable composition could form. Such a fluid was more stable than a pure methane fluid; therefore,
301 it could form at concentrations of C less than 2.4 m. The initial mineral reactants were 16.45 moles
302 of aragonite, 3.53 moles of antigorite, 0.71 moles of magnetite, and 1.88 moles of chlorite(ss) per
303 1,000 g of H_2O . The initial aqueous fluid/rock (F/R) mass ratio was 0.10. This ratio was the lowest
304 value tested and corresponded to 10.0 kg of rock and of a dilute initial aqueous fluid containing
305 1.0 kg of H_2O . The endpoint of the model was determined by the initial amount of H_2 with a value
306 of 66.5 moles per 1000 g of H_2O (Table 2). This value of H_2 resulted in the formation of
307 hydrocarbon fluids without secondary olivine(ss) appearance due to the reduction of magnetite.

308 The initial and final aqueous fluid compositions and mineral assemblages are shown in
309 Table 1 and the detailed mass transfer results are shown as a function of the logarithm of the

310 reaction progress ($\log \xi$) in Figs. 3A - E. Here, ξ represents the number of moles of H_2 added. The
 311 full reaction path output file is given in Appendix A. It can be seen in Fig. 3A that the reactant
 312 minerals, aragonite, antigorite, and magnetite were stable in the beginning, as these were used in
 313 the EQ3 code to develop the initial aqueous fluid chemistry, while chlorite(ss) increased with $\log \xi$.
 314 At a $\log \xi$ value of -1.37, clinopyroxene(ss) appeared consisting of almost pure diopside (95%)
 315 and minor hedenbergite (5%). The mole fraction of diopside decreased slightly to 90% until the
 316 end of the reaction (Table 1). Chlorite(ss) reached a plateau after $\log \xi$ of 0.28. Shortly after,
 317 brucite started to form, then antigorite and aragonite decreased strongly. Graphite then formed and
 318 increased until aragonite was totally destroyed; meanwhile, antigorite stopped decreasing. The
 319 graphitization could be expressed as the following reaction:



324 Finally, hydrocarbon fluid formed and completely replaced graphite. This reaction could be
 325 expressed as the reaction below:



327 The overall reaction of methane genesis was presented in Eqs. (1 and 2). The hydrocarbon
 328 fluid contained almost pure $CH_{4,f}$ (99.7%), as well as $C_2H_{6,f}$ (0.1%), $H_{2,f}$ (0.2%). Only trace
 329 amounts of $C_3H_{8,f}$ and $isoC_4H_{10,f}$ were produced. The amount of hydrocarbon fluid increased
 330 mainly during the final period of reaction progress ($\Delta \log \xi$ 0.21).

331 The change of mineral volumes can be seen in Fig. 3B. The volumes shown refer to 25°C
 332 and 0.1 MPa but these differ by less than about 3% from the volumes at 400°C and 2.0 GPa. For

333 the model system volume of in a $4,600 \text{ cm}^3$ ($3,800 \text{ cm}^3$ of reactant rock and 800 cm^3 of initial
334 aqueous fluid), the volumes show a dramatic destruction of antigorite and aragonite by about $1,680$
335 cm^3 and 560 cm^3 , respectively, while the other two reactants (magnetite and chlorite) were just
336 accessory minerals. In terms of product minerals, about $\sim 1,090 \text{ cm}^3$ of clinopyroxene(ss) and
337 $\sim 770 \text{ cm}^3$ of brucite were generated. Despite the significant number of moles of graphite formed,
338 the volume of graphite is small. The total volume of product minerals was about $\sim 380 \text{ cm}^3$ less
339 than the destroyed reactants. However, in addition to the mineral products, about 32.3 moles of
340 H_2O and 12.7 moles of fluid CH_4 were also produced (Table 2), which corresponded to about 487
341 cm^3 of H_2O and 332 cm^3 of fluid CH_4 , respectively (see also Fig. 4B below). Overall, the volume
342 of the system expanded by around 440 cm^3 . The reactions are self-promoting because more fluid
343 CH_4 formed at 2.0 GPa and $400 \text{ }^\circ\text{C}$ than lower pressures (Fig. 6A, see section 4.2.3).

344 The molalities of most dissolved elements showed only small changes as a function of
345 $\log \xi$ (Fig. 3C). Ca increased slowly and then decreased a little in the end. Fe decreased because
346 of the formation of clinopyroxene(ss). Then after clinopyroxene(ss) reached a peak, the reduction
347 of magnetite caused the decrease of Fe. Na, Cl, and Al did not participate significantly in any
348 reactions. However, the total dissolved C increased strongly with $\log \xi$ as aragonite progressively
349 dissolved. The molality of C reached a plateau when graphite formed, and the system was buffered.

350 Major changes in $\log f_{\text{O}_2}$ and $p\text{H}$ can be seen in Fig. 3D. The values of $\log f_{\text{O}_2}$ decreased
351 gradually then strongly, corresponding to the continuous addition of H_2 as a function of $\log \xi$. A
352 plateau was reached when graphite appeared, which buffered the $\log f_{\text{O}_2}$ co-existing with aragonite.
353 After all the aragonite was destroyed, the $\log f_{\text{O}_2}$ dropped quickly to the value where graphite and
354 hydrocarbon fluids (almost pure $\text{CH}_{4,f}$) could co-exist. The final $\log f_{\text{O}_2}$ was -30.2 (QFM -4.1).

355 The initial pH was very alkaline with significant amounts of Ca and Mg (Table 1). Overall, it was
356 a $Mg(OH)_2$ and $Ca(OH)_2$ solution. Interestingly, the pH became even more alkaline with $\log \xi$
357 as more Ca was added to the fluid by dissolution of aragonite (Fig. 3D). The rate of increase slowed
358 when clinopyroxene(ss) appeared, and then reached a peak after brucite appeared, resulting in
359 buffering of the pH at 5.80. The pH decreased a little to 5.77 corresponding to the formation of
360 the hydrocarbon fluids.

361 The change of concentrations of individual aqueous species mirrors the above changes in
362 the $\log f_{O_2}$, pH , and mineral products (Fig. 3E). It can be seen that $CH_{4,aq}^0$ was the most abundant
363 aqueous C-species and increased until graphite formed after which it increased again. These
364 changes correspond to the conversion of the carbonate in aragonite to graphite and then to methane.
365 The trends of the other aqueous hydrocarbon species were similar. Carbonate species decreased
366 all the way because of the drop of $\log f_{O_2}$. The molality of $H_{2,aq}^0$ did not increase much until the
367 last stage of the reaction progress where it only reached about 10 millimolal, which means that
368 almost all the reactant H_2 were consumed by incorporation into hydrocarbons as well as oxidation
369 to H_2O and OH -groups in brucite.

370 4.2.2 Models at 2.0 GPa and 400 °C with different initial F/R mass ratios

371 The standard model discussed above referred to an initial F/R ratio of 0.10 by weight. In
372 that model, the initial mass of rock was 10.0 kg and the initial fluid contained 1.0 kg H_2O (55.51
373 moles). We also investigated models with higher initial F/R for two reasons. First, the F/R of
374 natural samples are variable, and we could test differences in the model results if the decarbonation
375 reactions were extended. Second, higher F/R ratios might represent initial carbonated
376 serpentinites with a higher porosity. Third, higher F/R ratios imply less amounts of initial

377 aragonite relative to 1.0 kg H_2O , which in turn requires less H_2 to destroy the aragonite and
378 facilitate the formation of hydrocarbon fluids.

379 Models of four additional initial F/R ratios were calculated ranging from 0.10 to 0.63 and
380 corresponding initial amounts of reactant H_2 from 66.5 moles to 10.6 moles, respectively (Table 2
381 and Figs. 4A and B). All the models finished before the formation of olivine(ss). The mass ratios
382 of H_2 and rock were very similar for all the runs, around 0.0133 (Table 2 and Fig. 4A).
383 Interestingly, even with a wide range of F/R ratios, the predicted mineral sequences, solid solution
384 compositions, hydrocarbon fluid compositions, $\log f_{O_2}$, pH , trends of dissolved elements and
385 aqueous species were all very similar to the standard run described above. The absolute amounts
386 of minerals and hydrocarbon fluids decreased with higher F/R ratios. Less H_2O formed during the
387 reactions (from 32.3 to 5.57 moles) so the concentration of elements and aqueous species were
388 lower than the standard run (Fig. 4B).

389 The formation of hydrocarbon fluids decreased by 2 log units corresponding to the rise in
390 F/R from 0.10 to 0.63 (Table 2, Fig. 4B). The mass of rock after reaction decreased in every run.
391 In the standard run, the mass of rock decreased by 7.30%. The percentage of decrease was slightly
392 greater in runs with higher F/R (8.18%). Taking into account the final amounts of H_2O , the final
393 values of F/R could be calculated, and they were higher than the initial F/R ratio because of the
394 significant number of moles of excess H_2O created during the mass transfer. The percentage of
395 increase was 10% for the initial F/R ratio of 0.63, but reached 59% for the initial F/R ratio of
396 0.10. To conclude, lowering the F/R increased the formation of the immiscible hydrocarbon fluids
397 significantly because of the reduction of large amounts of aragonite. Because of the extra H_2O
398 formed, the aqueous fluids were diluted by the oxidation of H_2 fluids and $CH_{4,aq}^0$ was the only
399 major aqueous carbon species.

400 4.2.3 Models at different temperature-pressure conditions

401 To investigate the roles of temperature and pressure during the formation of hydrocarbons
402 from the reduction of carbonated serpentinite, we expanded our conceptual model at pressure and
403 temperature conditions along the metamorphic path of the Lanzo Massif (Vitale Brovarone *et al.*
404 2017, Giuntoli *et al.* 2020). The pressure and temperature conditions run with the mass transfer
405 model were 1.0 GPa and 400 °C, 1.5 GPa and 400 °C, 2.0 GPa and 450 °C, and 2.0 GPa and 500 °C
406 (Figs. 5, 6, & 7, Table S-1 to S-4) with a F/R mass ratio of 0.1. The rock reactants were the same
407 for each run: 16.45 moles of aragonite, 3.53 moles of antigorite, 0.71 moles of magnetite, and 1.88
408 moles of chlorite(ss). However, the numbers of moles of H_2 needed were 68.4, 66.4, 53.9, and
409 76.8, respectively, depending on the reaction conditions. At 1.5 GPa and 400 °C, the amount of
410 H_2 corresponds to the point just before olivine(ss) formation, the same as the standard run at 2.0
411 GPa and 400 °C. However, at 1.0 GPa and 400 °C, 2.0 GPa and 450 °C, and 2.0 GPa and 500 °C,
412 the number of moles of H_2 corresponds to the point when 1.0 mole of hydrocarbon fluids formed
413 because olivine(ss) formed before hydrocarbon fluids.

414 The lowest pressure considered, 1.0 GPa and 400 °C, was on the exhumation path, other
415 conditions were on the prograde path of the Lanzo massif (Vitale Brovarone *et al.* 2017). Figure 5
416 presents the amounts of minerals, both reactants and products, as a function of $\log \xi$. Antigorite
417 was stable in the beginning and then decreased at all conditions. Because of the large molecular
418 formula of antigorite, the destroyed volume of antigorite reached about 1,800 cm^3 (37% of the
419 total volume in the system). Clinopyroxene(ss) was the first product mineral with almost pure
420 diopside and then brucite formed in all the runs. Chlorite(ss) with more than 95 mol% clinochlore
421 did not react and stayed until the end of the runs, except for a slight decrease at 1.0 GPa and 400 °C.
422 Hydrocarbon fluids formed during a late interval of reaction progress and increased quickly.

423 At 1.0 GPa and 400 °C, calcite(ss) was more stable than aragonite (Fig. 5A, Table S-1).
424 Interestingly, this, the retrograde path model, was the only model without graphite formation.
425 Hydrocarbon fluids formed directly from calcite(ss). As mentioned above, graphite is not stable
426 relative to aragonite for certain levels of the ratio $a_{Ca^{2+}}/a_{H^+}^2$ in the aqueous phase. At this pressure
427 and temperature, graphite cannot be stable when the aqueous fluid has a $\log(a_{Ca^{2+}}/a_{H^+}^2)$ value
428 less than 9.50. In the run shown in Fig. 5A, the value of $\log(a_{Ca^{2+}}/a_{H^+}^2)$ changed from an initial
429 value of 9.29 to a final value of 9.46. Fe-rich olivine(ss) with $X_{Fayalite}$ 0.29 formed near the endpoint
430 and increased rapidly to 3.8 moles before hydrocarbons appeared.

431 The model at 1.5 GPa and 400 °C (Fig. 5B, Table S-2) was similar to the standard model
432 at 2.0 GPa and 400 °C in terms of the mineral sequence, the relative amounts of minerals, and the
433 amount of H_2 reactant. However, the model at 2.0 GPa and 450 °C (Fig. 5C, Table S-3) showed
434 the same mineral sequence as the standard model until magnetite was totally consumed and then
435 olivine(ss) formed before the formation of hydrocarbon fluids. The olivine was Fe-rich ($X_{Fayalite}$
436 0.26), representing a metasomatic composition. It appeared that the breakdown of magnetite
437 caused by the addition of H_2 provided Fe^{2+} that stabilized olivine. If more H_2 was added, olivine
438 became unstable and was reduced to metallic iron. The amount of H_2 (53.9 moles) used here
439 represents the value when 1.0 mole of hydrocarbon formed co-existing with graphite. Graphite
440 was completely destroyed for values of H_2 equal to or more than 66.5 moles.

441 Interestingly, our model at 2.0 GPa and 500 °C (Fig. 5D, Table S-4) contained olivine with
442 antigorite throughout the reaction progress. As magnetite started to decrease sooner in this model,
443 the formation of olivine(ss) was even more strongly favored, and it became the most abundant
444 mineral quickly. When magnetite was destroyed, the iron content of the olivine reached a peak at
445 Fa 21, but then the rate of olivine increase slowed. Forsterite started to increase and finally reached

446 the upper mantle composition (Fo 93). If more H_2 was added, even up to 90.0 moles, no metallic
447 iron formed and the hydrocarbon fluids ended up very H_2 -rich. Calcite(ss) was more favored than
448 aragonite at this condition and was reduced to form graphite and then hydrocarbon fluids. Graphite
449 formed only slightly before brucite.

450 In order to investigate the effect of magnetite destruction on the formation of olivine(ss),
451 we tested models without magnetite as a reactant. At 2.0 GPa and 450 °C, without reactant
452 magnetite in the initial rock, we found that only a very small amount of magnetite formed and then
453 disappeared during the run (Fig. 5E). The log number of moles of magnetite was -5.7 to -5.0 during
454 $\log \xi$ from -3.8 to -2.6. This small amount of magnetite simply reflected the (low) amount of Fe
455 in the initial fluid. No olivine formed. However, for the model at 2.0 GPa and 500 °C also without
456 magnetite, a very small and transient amount of olivine(ss) appeared (Fig. 5F), but at a much later
457 stage of reaction progress than in Fig. 5D at the same pressure and temperature. Only 0.056 moles
458 of olivine(ss) formed from $\log \xi$ at 0.20 - 0.28 and then disappeared. No extra olivine(ss) formed
459 even if more H_2 was added. The excess H_2 stayed in the hydrocarbon fluids at 2.0 GPa and 500 °C
460 and the hydrocarbon fluids became H_2 -rich. Clearly, the absence of magnetite as a reactant had a
461 strong effect in inhibiting olivine(ss) formation at both 450 and 500 °C. We note that in the natural
462 samples, no preserved olivine was observed. The reason for this discrepancy may lie in the highly
463 heterogeneous nature of the Lanzo carbonated serpentinite or to retrograde hydration. If H_2 fluid
464 pathways did not encounter magnetite, or the amount of magnetite encountered was very low, our
465 models show that olivine would not be expected to form to a significant extent.

466 Hydrocarbon fluids formed at the end of the reactions at each pressure and temperature
467 condition are presented in Figs. 5A - F. The final amounts and compositions of the hydrocarbon
468 fluids can be seen in Fig. 6 over the range of 1.0 - 2.0 GPa and 350 - 500 °C. At the higher pressures

469 and lower temperatures, if olivine(ss) did not form, hydrocarbon fluid formation was favored (Fig.
470 6A). The reason is simply that the saturation activity of $CH_{4,aq}$ was smaller at higher pressure and
471 lower temperature. In models without magnetite, more hydrocarbons formed, and the degree of
472 increase is greater at higher temperature. Except for the models at 2.0 GPa, 450 °C and 500 °C,
473 the amounts of H_2 were about 66.0 moles. If the saturation activity of $CH_{4,aq}^0$ were smaller (i.e. the
474 solubility was lower), more $CH_{4,f}$ could equilibrate in hydrocarbons.

475 The fluid compositions shown in Fig. 6B indicate that $CH_{4,f}$ was the most abundant
476 endmember of the immiscible fluids over the temperature range considered. Except at 2.0 GPa and
477 500 °C, the hydrocarbon was almost pure $CH_{4,f}$ with a mole fraction larger than 0.90. At 2.0 GPa,
478 from 450 °C to 500 °C, the mole fraction of $CH_{4,f}$ dropped from 0.99 to 0.65 as the $H_{2,f}$
479 component increased up to 0.35. However, other hydrocarbons were negligible. At 1.0 GPa, the
480 mole fraction of $H_{2,f}$ was much greater than at higher pressures at 400 °C. No significant effect on
481 the composition of fluids by pressure was observed. Overall, the fluids were methane-rich without
482 olivine. If more initial H_2 were added, the curves would move towards more H_2 -rich compositions.
483 After all the carbon was reduced by the reactant H_2 , the $H_{2,f}$ became unreactive and built up as a
484 component in the hydrocarbon fluid.

485 The final $\log f_{O_2}$ at each condition with an F/R equal to 0.1 is given relative to the QFM
486 buffer in Fig 7A. The highest $\log f_{O_2}$ was at 2.0 GPa and 450 °C because hydrocarbon fluids
487 formed coexisting with graphite with the lowest initial number of H_2 moles. The $\log f_{O_2}$ at 400 °C
488 of both 1.5 and 2.0 GPa were very close, as were the other results for minerals, aqueous species,
489 and hydrocarbon compositions at these conditions. At 2.0 GPa and 350 °C, the $\log f_{O_2}$ was lower
490 probably because olivine(ss) was not favored at low temperature and only formed at temperatures

491 greater than 400 °C. The models at 500 °C had the largest initial number of H_2 moles. This large
492 amount of H_2 resulted in the total reduction of oxidized C and the excess H_2 caused extremely
493 reducing conditions (Fig. 7A). The final $\log f_{O_2}$ values of the models were not affected
494 significantly by removing magnetite as a reactant.

495 The final pH value of each model (relative to neutral pH) with F/R equal to 0.1 is plotted
496 in Fig. 7B. It can be seen that the final ΔpH values increased less than 0.2 compared to the initial
497 pH values. The fluids are basically $Mg-Ca-OH$ fluids. All of the fluids were alkaline because
498 brucite was in equilibrium with the aqueous fluids, and contributed to Mg^{2+} and OH^- . At 2.0 GPa,
499 the final pH decreased with temperature resulting in less alkaline aqueous fluids. The final Ca
500 concentrations were observed decreasing from 0.038 to 0.021 molal with temperature at 2.0 GPa
501 (Table S1-4). Lower Ca concentrations resulted in lower values of the pH . At 400 °C, the final pH
502 increased from 1.0 to 2.0 GPa. The opposite trend of Ca concentration showed that Ca increased
503 from 0.008 to 0.031 molal with pressure at 400 °C. Interestingly, the drop of pH was affected more
504 by temperature even when Ca decreased by 0.017 molal. Again, the final pH values of the models
505 were not affected by removing magnetite from the reactants.

506 Overall, the above models demonstrated that hydrocarbons could form over a wide range
507 of pressure and temperature conditions, during both the prograde metamorphism and exhumation
508 processes of the Lanzo Massif (Vitale Brovarone *et al.* 2017). The process of hydrocarbon
509 formation was systematically the same as the standard model within the pressure range of 1.5 to
510 2.0 GPa and a temperature range of 400 to 450 °C. The product minerals diopside, brucite, and
511 graphite were consistent with the natural samples at 1.5 to 2.0 GPa. Our model with expanded
512 pressure and temperature conditions predicted small variations of mineral assemblages and
513 hydrocarbon compositions.

514 4.2.4 Garnet formation

515 The model results presented above could reproduce with a good confidence level the
516 natural features described by Vitale Brovarone et al. (2017). However, in other samples from the
517 same locality, Giuntoli et al. (2020) also reported the presence of Ca-Fe-rich garnet forming along
518 carbonate reduction channels. The formation of Ca-Fe-rich garnet was not predicted by our models
519 for low carbonate/serpentinite ratios (15 vol.% aragonite; 85 vol.% serpentinite) at 2.0 GPa and
520 400°C provided that we chose an appropriate standard Gibbs free energy of andradite less stable
521 than that reported by Moecher and Chou (1990). However, using the same characterization of
522 andradite, Ca-Fe-rich garnet did form at 2.0 GPa and 400°C when we performed complementary
523 models for two higher carbonate/serpentinite ratios (30 vol.% aragonite, 70 vol.% serpentinite; and
524 50 vol.% aragonite, 50 vol.% serpentinite) consistent with the results described by Giuntoli et al.
525 (2020). In these latter two models, the final mineral assemblage, after antigorite and chlorite were
526 exhausted, brucite, clinopyroxene, aragonite, graphite, and Ca-rich-garnet together with
527 hydrocarbon fluid (see Appendix A).

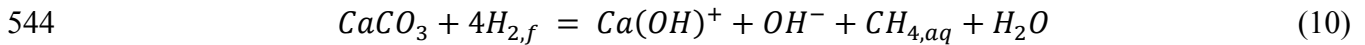
528 5. Discussion

529 5.1 Comparison of model results with the altered Lanzo carbonated serpentinites

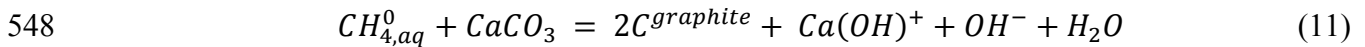
530 Our study has established predictive models of the formation of immiscible hydrocarbon
531 fluid during the reaction of H_2 with carbonated serpentinite at temperatures and pressures relevant
532 to subduction zones. Here we compare the model results with the previously reported petrographic
533 results in Vitale Brovarone et al. (2017). As summarized above in Section 2, the overall reaction
534 suggested for the carbonated serpentinite reduction and hydrocarbon formation as in Eq. (1)
535 indicates that antigorite and Ca-carbonate reacted with H_2 to form clinopyroxene, brucite, methane,

536 and water. The results for our standard model (Fig. 3) agree with this generalized reaction.
537 However, the generalized reaction does not capture all the petrographic detail.

538 For example, the natural samples contain evidence that Ca-carbonate was first reduced to
539 methane and graphite and then graphite was altered to methane during protracted H₂ infiltration
540 (Vitale Brovarone *et al.* 2017). A recent experimental study is consistent with the proposed latter
541 process (Peña-Alvarez *et al.* 2021). An overall reaction for alteration of Ca-carbonate to graphite
542 was already given in Eqs. (7) and (8). Here we present more detail. In most of our models, Ca-
543 carbonate was first reduced to CH_{4,aq} by H₂, which can be expressed as



545 This reaction contributes to the early increases in *pH* and CH_{4,aq}⁰ seen in Figs. 3D and E. The
546 *logf*_{O₂} continued to decrease and *a*_{CH_{4,aq}} increased to reach the equilibrium between CH_{4,aq}⁰ and
547 graphite, coexisting with the reactant Ca-carbonate, which can be expressed by



549 During the co-existence of aragonite and graphite, *logf*_{O₂} was buffered (Fig. 3D). But with even
550 more H₂ reacting, eventually the aragonite was completely destroyed and the *logf*_{O₂} dropped
551 associated with an increase in the *a*_{CH_{4,aq}}⁰. In turn, these changes destabilized graphite in favor of
552 CH₄-rich fluid according to Eq. (9) above. In this way, the model predicted the formation of
553 graphite from aragonite, and subsequently the formation of immiscible hydrocarbon fluid from
554 graphite. The model prediction is therefore in agreement with the data for the natural samples with
555 regard to an important sequence of events.

556 Another way to compare the model results with the natural samples is to examine the fluid
557 chemistry. The fluid inclusions reported for the altered carbonated serpentinite (Section 2) were

558 mostly CH_4 - H_2 -rich (plus minor ethane), associated with graphite rims on serpentinite clasts.
559 Minor amounts of H_2O -bearing inclusions were related to graphite-free serpentinite clasts. The
560 first type is approximated by our model immiscible hydrocarbon fluid. At 2.0 GPa and 400 °C, the
561 model fluid is predominantly CH_4 with minor H_2 and very minor amounts of ethane as the second
562 most abundant hydrocarbon. Despite the approximations in our model regarding ideal solution in
563 the hydrocarbon fluid, the above results are reasonably consistent with the actual fluid inclusions.
564 The H_2O -bearing fluid inclusions associated with graphite-free partially reacted carbonated
565 serpentinites, could represent an early stage in our models with higher $\log f_{O_2}$ and lower $a_{CH_4, aq}$.

566 **5.2 Carbon and Hydrogen budget during hydrocarbon formation**

567 In all our models, the carbon in the initial system is almost entirely present in the
568 carbonated serpentinites as a carbonate mineral. In the standard model at 2.0 GPa and 400 °C,
569 when hydrocarbon fluid first appeared at $\log \xi$ of 1.61, the carbon budget in moles was 76.5%,
570 0.2%, and 23.3% of graphite, hydrocarbon, and aqueous carbon, respectively. Graphite then
571 dropped to only 9.3%, whereas hydrocarbons increased to 67.5%, and aqueous carbon remained
572 about the same. In the final step, the hydrocarbon fluid contained 77.1% and aqueous carbon
573 contained 22.9% of the total carbon.

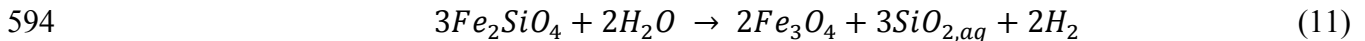
574 The budget of hydrogen (H) is also important because H from the influx of $H_{2,f}$ can be
575 incorporated into antigorite and brucite, as well as aqueous and hydrocarbon fluids. The H in the
576 initial system before $H_{2,f}$ reacted was almost all in antigorite and the initial water. The mole
577 percentages were 49.6 % and 50.4 %, respectively.

578 However, the final hydrogen budget (Table 3) shows that H_2O still took up nearly half of
579 the H even after 66.5 moles of $H_{2,f}$ were added to the system. A lot of H_2O formed during the

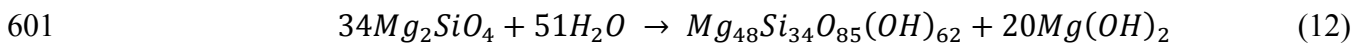
580 reactions and brucite was the second most abundant species containing 17.7% of the total H_2 .
 581 Antigorite contained only 14.1%. Methane in the hydrocarbon fluid constituted 14.4% of the total
 582 hydrogen, but $CH_{4,aq}$ constituted only 4.2% of the total hydrogen. Compared with the carbon
 583 budget, the hydrogen budget was more complex because multiple types of H-bearing species
 584 existed in models at all temperature-pressure conditions, and were not affected by the carbon
 585 mineral sequences, although the percentages varied. Overall, both the carbon and hydrogen
 586 budgets were useful tools for tracking the redox reactions systematically.

587 ***5.3 Origin of H_2 fluids that reacted with carbonated serpentinites in the Lanzo Massif***

588 The origin of the large amounts of H_2 fluid involved in the alteration of the Lanzo
 589 carbonated serpentinites is an interesting topic. It has been suggested that the H_2 could have
 590 originated by serpentinization of the fresh peridotite rocks in the massif during subduction and
 591 then migrated along channelized fluid pathways (Debret *et al.* 2013, Vitale Brovarone *et al.* 2017,
 592 2020). Typically, H_2 can be generated by the oxidation of the fayalite endmember in primary
 593 peridotitic olivine, which can be expressed as



595 The above reaction enables an estimate of the amount of olivine that would need to be
 596 serpentinized to provide all the H_2 for making CH_4 . For example, at 2.0 GPa and 400 °C, 66.5
 597 moles of $H_{2,f}$ were needed to form 12.7 moles of $CH_{4,f}$. According to Eq. (11), 99.75 moles of
 598 fayalite would be needed. If we assume that the mole fraction of fayalite in the peridotitic olivine
 599 was 7%, then 1,325 moles of forsterite should be serpentinized. Using the following
 600 serpentinization reaction



602 the 1,325 moles of forsterite should produce 39 moles of antigorite. Overall, to form 66.5 moles
603 of $H_{2,f}$ (around 903 cm^3) and 12.7 moles of $CH_{4,f}$, about 0.06 m^3 of olivine were destroyed and
604 about 0.07 m^3 of antigorite were created. These quantities of minerals are small compared to the
605 amounts available in a massif.

606 CH_4 - H_2 -rich fluid inclusions have also been found in the high-pressure serpentized
607 ultramafic peridotites of other subduction zone complexes (Vitale Brovarone *et al.* 2020, Boutier
608 *et al.* 2021). Additional reduced fluid species such as H_2S and NH_3 were found in some of the
609 preserved inclusions. The condition of high-pressure serpentization happened near the peak
610 metamorphic condition, 370 - 400 °C and 1 GPa for the eclogitic-facies Lanzo massif. Graphitic
611 carbon was not commonly observed, which was consistent with our model at those temperature
612 and pressure conditions (Fig. 5A). The $\log f_{O_2}$ of serpentization was inferred to be less than
613 QFM because awaruite was associated with antigorite. CH_4 in the fluid inclusions was thought to
614 have been formed by reduction of carbon in the serpentizing fluid.

615 **6. Conclusions**

616 We have focused on predicting the formation of immiscible hydrocarbon fluids at upper
617 mantle conditions. We set up initial aqueous speciation and solubility models in equilibrium with
618 carbonated serpentinite consistent with the natural samples reported by Vitale Brovarone *et al.*
619 (2017) and Giuntoli *et al.* (2020). The initial fluids were then used in chemical mass transfer
620 models simulating the irreversible reactions during the reduction of carbonated serpentinites by
621 invading H_2 fluids. Immiscible hydrocarbon fluids formed in association with major changes of
622 mineralogy and aqueous solution chemistry. The models covered a pressure-temperature range of
623 1.0 - 2.0 GPa and 350 - 500 °C.

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We found the following principal results from this modeling study:

- Chemical mass transfer models predicted minerals and hydrocarbon fluids consistent with field and laboratory observations in Vitale Brovarone et al. (2017) and Giuntoli et al. (2020):
 - a) Serpentinite (antigorite, magnetite, and chlorite) and aragonite were destroyed.
 - b) Brucite, clinopyroxene(ss), graphite, and immiscible hydrocarbon fluids were formed at 1.5 and 2.0 GPa and 400 - 500 °C.
 - c) For high initial carbonate/serpentinite ratios, Ca-Fe-rich garnet was formed at 400°C and 2.0 GPa.
 - d) Methane was the main constituent of the immiscible hydrocarbon fluids and also reached molal concentrations in the coexisting aqueous fluids.
- As an example, the reaction progress during our standard run at 2.0 GPa and 400 °C with F/R mass ratio of 0.10 revealed the sequence of mineral formation, the number of moles and volumes of each mineral, the aqueous fluid composition and speciation, and the evolution of the $\log f_{O_2}$ and pH . During the reactions, aragonite was reduced by H_2 to form graphite and then graphite was reduced to hydrocarbon fluid (almost pure $CH_{4,f}$) associated with an almost continuous drop of $\log f_{O_2}$.
- The reaction of H_2 with carbonated serpentinite generated significant amounts of H_2O .
- Lower F/R (aqueous fluid/rock) ratios imply more H_2 fluids, which resulted in greater amounts of H_2O and hydrocarbon fluids formed.
- At 1.0 GPa and 400 °C, graphite was not stable due to the $\log(a_{Ca^{2+}}/a_{H^+}^2)$ of the system being too low.

- 646 • Even small amounts of magnetite in the initial rock caused olivine(ss) to appear before
647 hydrocarbon formation in models at 1.0 GPa and 400 °C, 2.0 GPa and 450 °C, and 2.0 GPa
648 and 500 °C. Olivine was not stable if the reactant carbonated serpentinite did not contain
649 magnetite.
- 650 • Carbon and hydrogen budgets trace the transfer and redistribution of these elements during
651 the redox reactions.
- 652 • Overall, the combined results of the modeling study and the natural samples strongly
653 support the concept that CH_4 -rich immiscible hydrocarbon fluids have formed at eclogite
654 facies conditions in subduction zones. How widespread this phenomenon is (at the present
655 and in the geologic past) remains to be seen.

656

657 **Data Availability:**

658 The files of the model results are available on Johns Hopkins Research Data Repository
659 using the DOI given below. The data can be referred to using the citation below.

660 Huang, Jingyi; Sverjensky, Dimitri A.; Daniel, Isabelle; Brovarone, Alberto Vitale, 2022,
661 "Data associated with: Reaction path model of the formation of abiotic immiscible hydrocarbon
662 fluids in subducted carbonated serpentinites, Lanzo Massif (Western Italian Alps)",
663 <https://doi.org/10.7281/T1/NLHSKE>, *Johns Hopkins Research Data Repository*.

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672 **Appendix A. Supplementary Material**

673 The supplementary material contains the description of model files and tables about the
674 summary of the initial and final fluid compositions and mineral assemblages. The files contain
675 model results of H_2 fluid reacting with carbonated serpentinites with 15 vol% of aragonite and 85
676 vol% of serpentinite at 2.0 GPa and 400 °C, 1.0 GPa and 400 °C, 1.5 GPa and 400 °C, 2.0 GPa
677 and 450 °C, and 2.0 GPa and 500 °C; with 30 vol% of aragonite and 70 vol% of serpentinite at
678 400°C and 2.0 GPa; and with 50 vol% of aragonite and 50 vol% of serpentinite at 400°C and 2.0
679 GPa.
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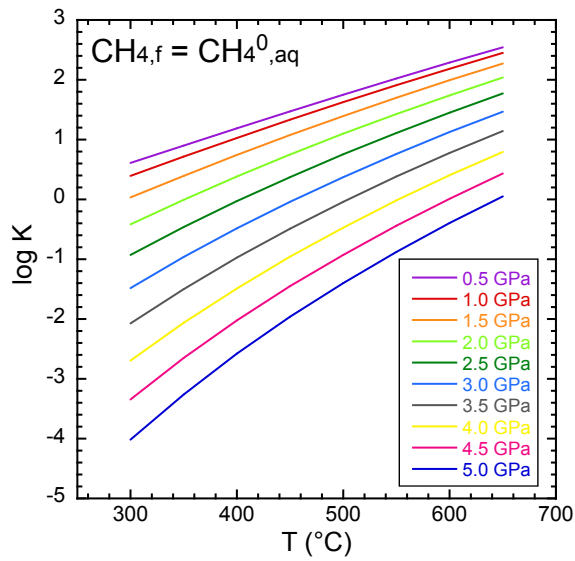
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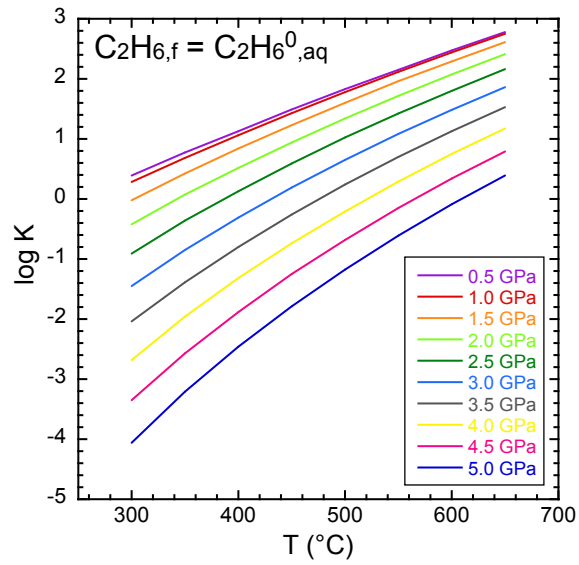
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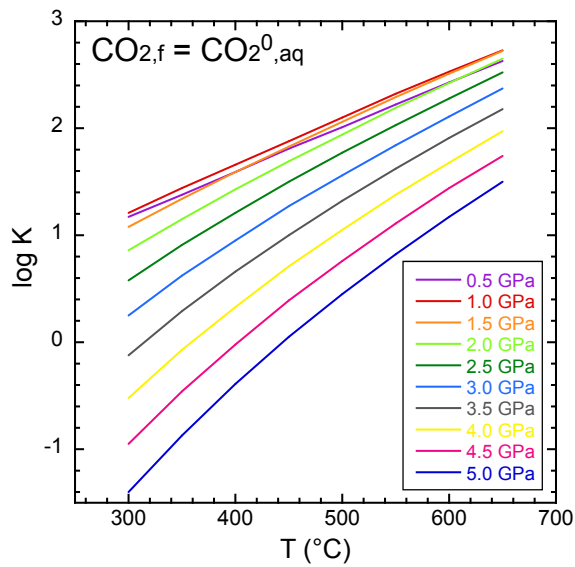


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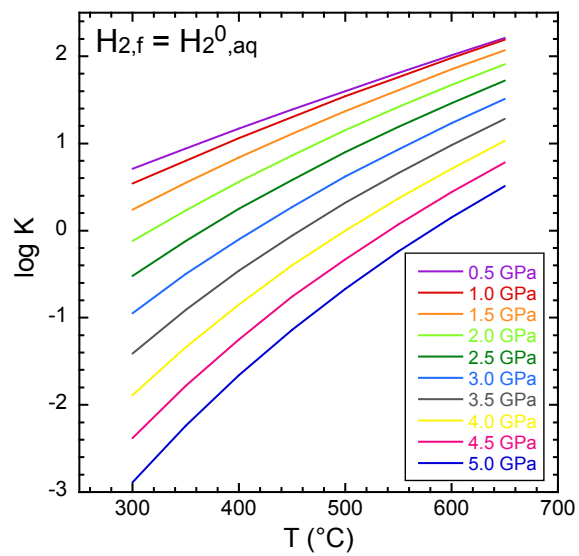


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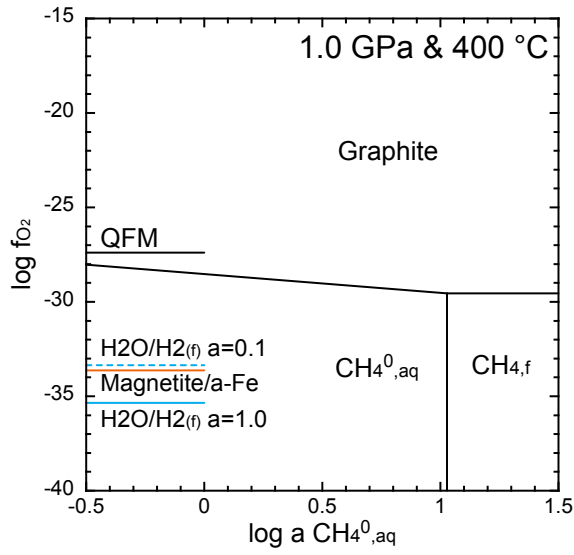


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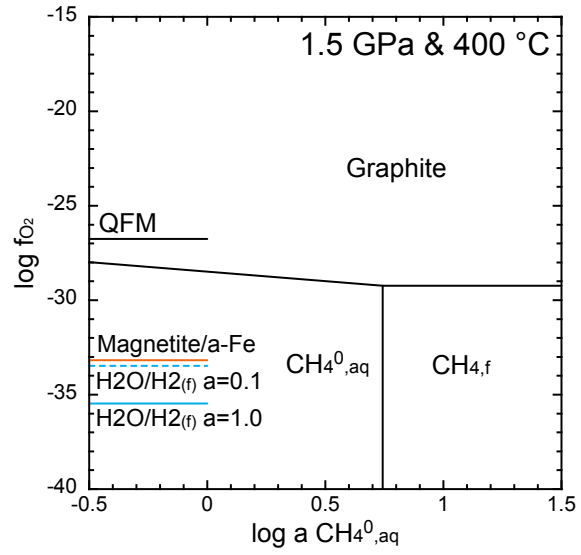
5 **Figure 1.** *Log K* of reactions of fluid species and aqueous species. (A) CH_4 , (B) C_2H_6 , (C) CO_2 ,6 and (D) H_2 .

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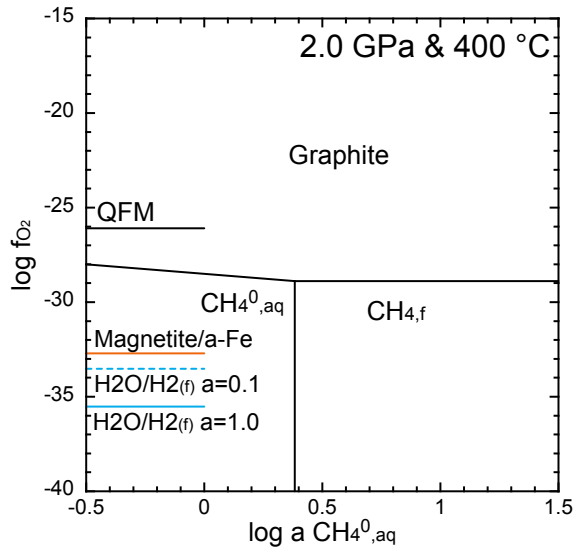


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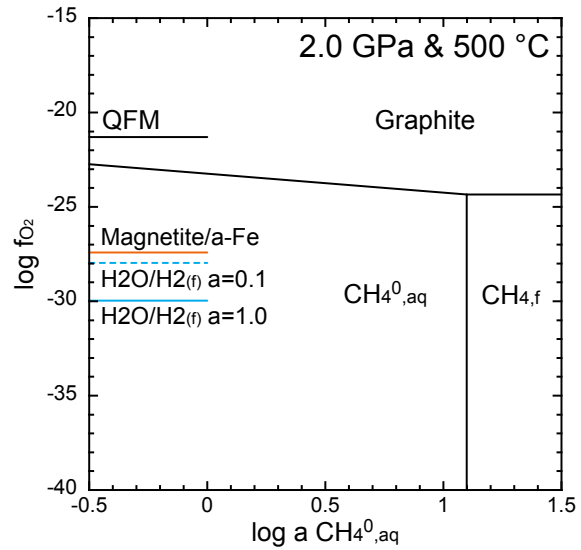


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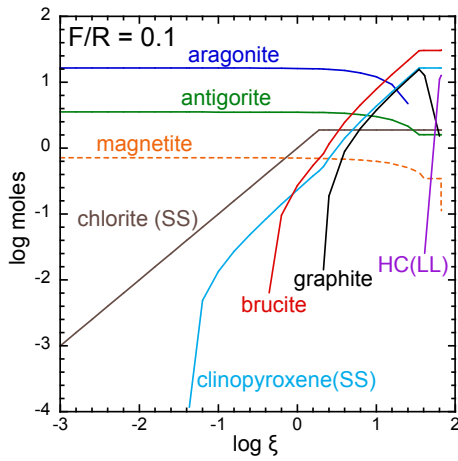


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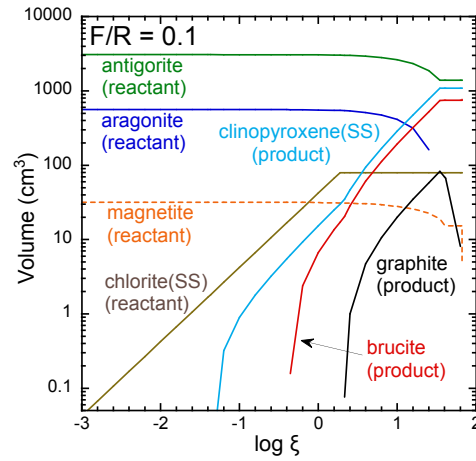
12 **Figure 2.** $\log f_{O_2}$ vs. $\log a_{CH_4^0,aq}$ diagrams of the stability field among graphite, CH_4^0,aq , and
 13 $CH_{4,f}$ at (A) 1.0 GPa & 400 °C, (B) 1.5 GPa & 400 °C, (C) 2.0 GPa & 400 °C, and (D)
 14 & 500 °C.

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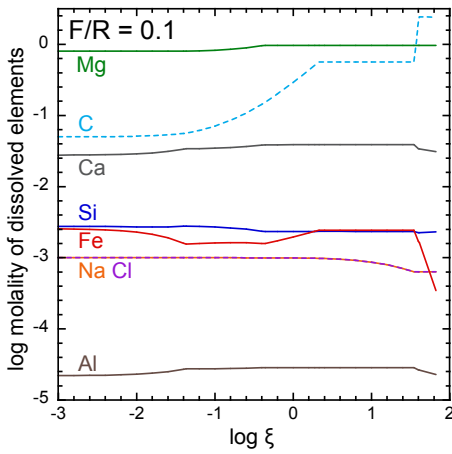
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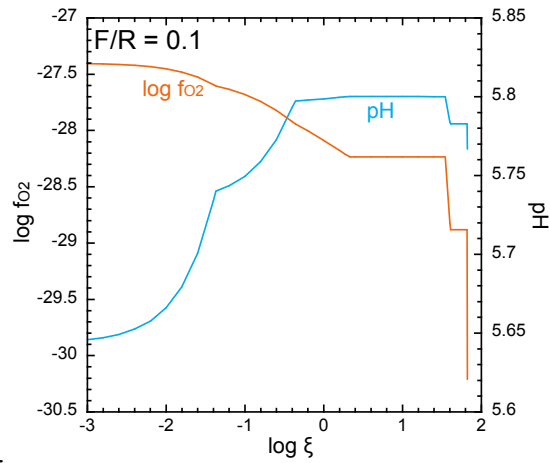
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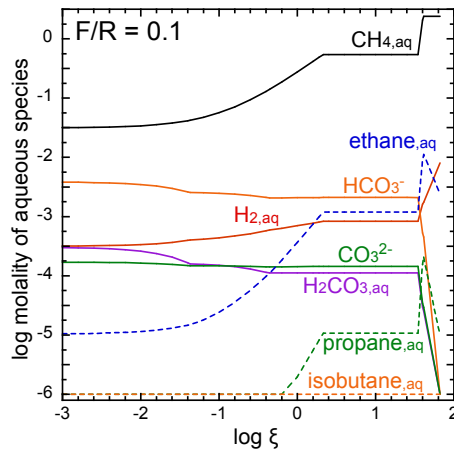


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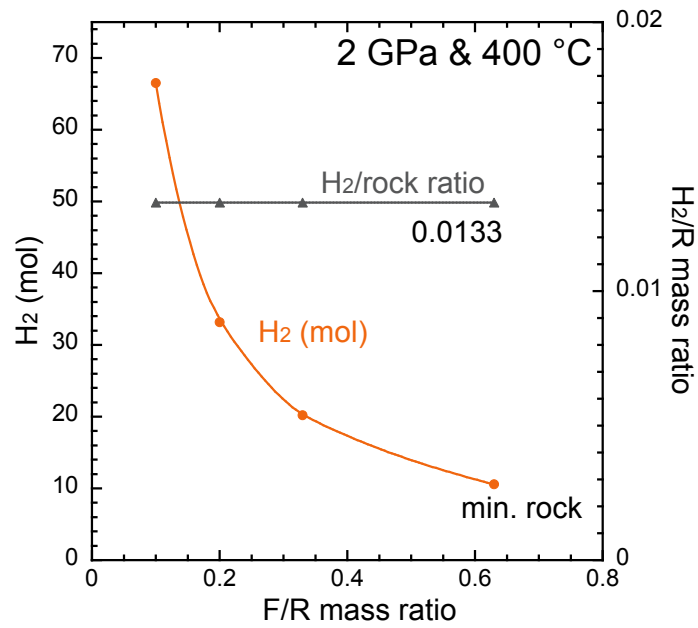


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20 **Figure 3.** Reaction path model of the reduction of carbonated serpentinite by H_2 at 2.0 GPa and
 21 400.0 °C with F/R equal to 0.1 (by weight) as a function of the logarithm of the reaction progress
 22 ($\log \xi$): (A) minerals and hydrocarbon fluid, (B) volumes of minerals, (C) dissolved elements, (D)
 23 $\log f_{O_2}$ and pH , and (E) aqueous species.

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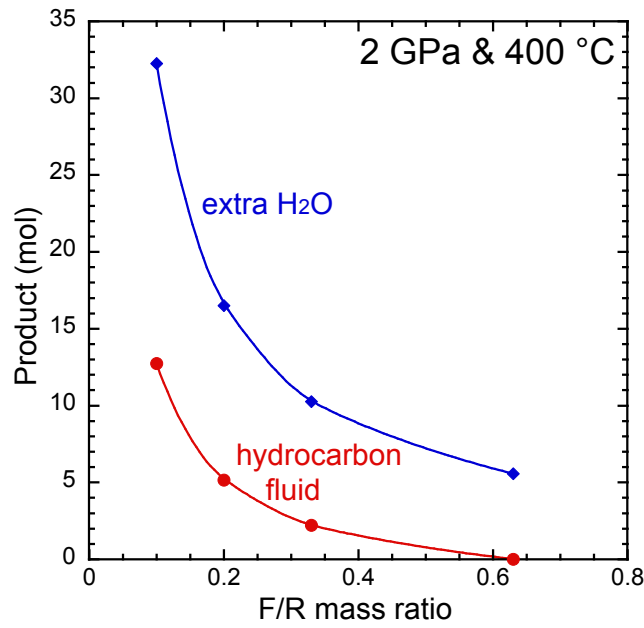
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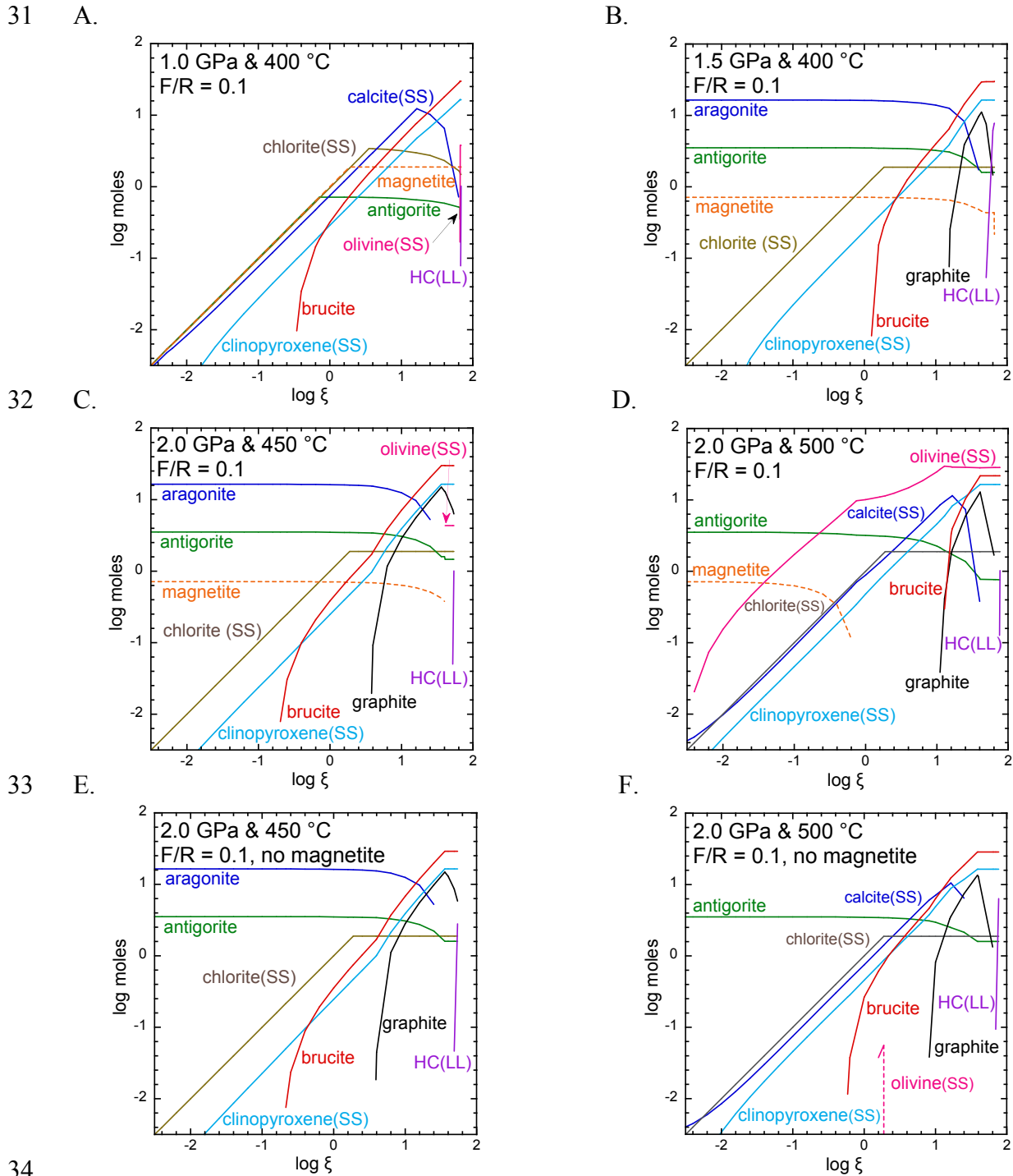


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28 **Figure 4. (A)** Number of moles of H₂ consumed and the H₂/R mass ratio vs. F/R mass ratio; **(B)**

29 Number of moles of immiscible hydrocarbon fluids and excess H₂O formed vs. F/R mass ratio.

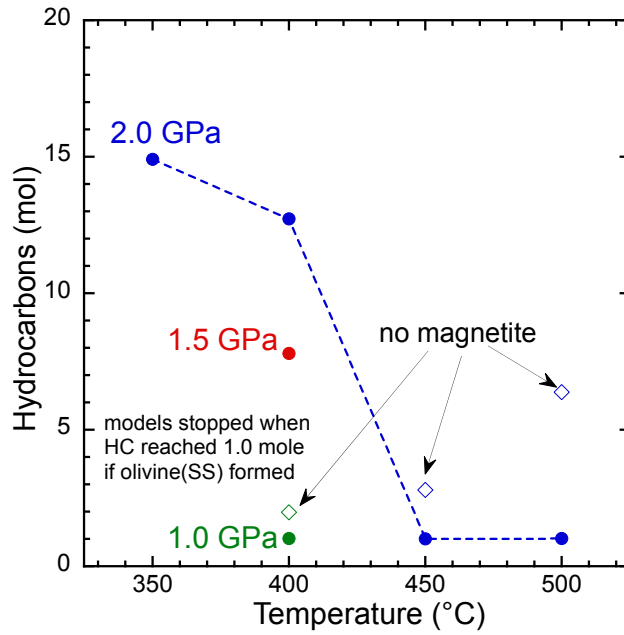
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34
 35 **Figure 5.** Reaction path models of the destruction of carbonated serpentinites by H_2 at different
 36 temperatures and pressures with F/R equal to 0.1 (by weight). The logarithms of the number of
 37 moles of minerals produced are shown as functions of $\log \xi$: (A) 1.0 GPa and 400 °C; (B) 1.5 GPa
 38 and 400 °C; 2.0 GPa and (C) 450 °C, (D) 500 °C; 2.0 GPa and (E) 450 °C, (F) 500 °C GPa without
 39 initial reactant magnetite.

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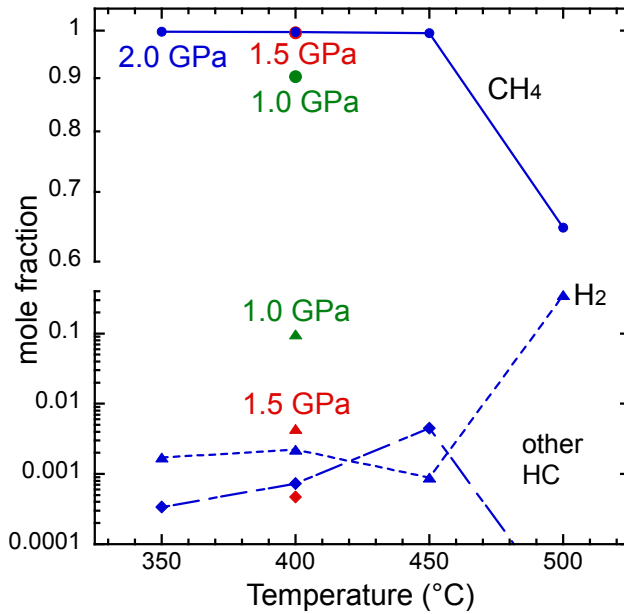
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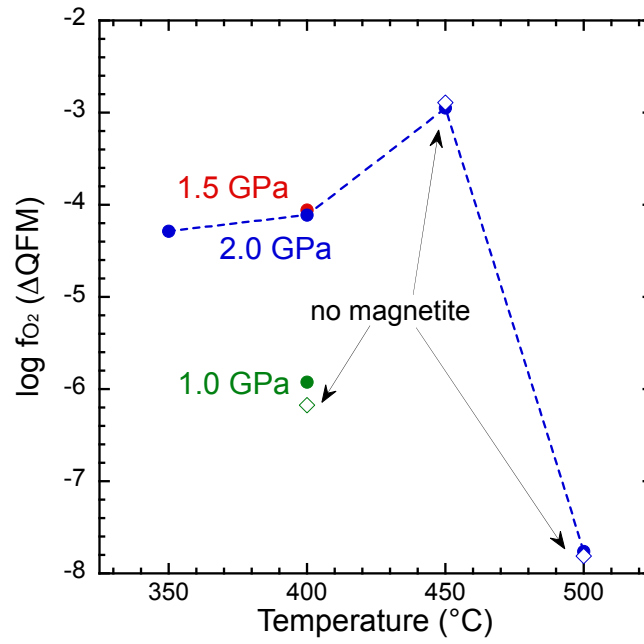


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44 **Figure 6. (A)** Number of moles of hydrocarbon fluids and **(B)** mole fractions of fluid hydrocarbon
 45 species vs. temperature at 1.0 (green), 1.5 (red), and 2.0 (blue) GPa. **(A)** Models without magnetite
 46 are represented by empty diamonds. **(B)** The dots and solid line represent CH_4 , the triangles and
 47 dashed line represent H_2 , and the diamonds and dash-dotted line represent other hydrocarbons (see
 48 text).

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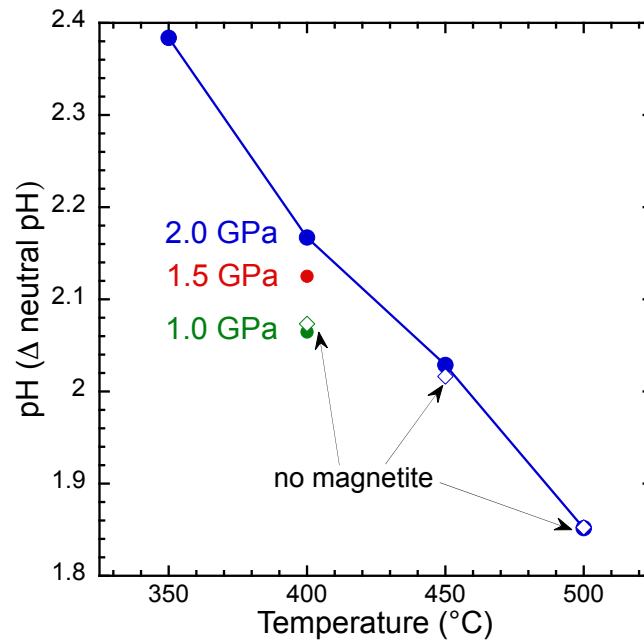
A.



50

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B.



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53 **Figure 7. (A)** $\log f_{O_2}$ relative to QFM and **(B)** pH relative to neutral pH vs. temperature at the
54 end of the reactions with F/R 0.1 at 1.0 GPa (green), 1.5 GPa (red), and 2.0 GPa (blue). Models
55 without magnetite are represented by empty diamonds.

1 **Table 1.** Summary of the initial and final fluid compositions and mineral assemblages at 400 °C
 2 and 2.0 GPa with F/R 0.1. Full details of the aqueous speciation of all the elements at each step
 3 of the reaction progress are given in the reaction path output file (see File 1 in Appendix A).

INITIAL FLUID	Parameter value ^a		FINAL FLUID	Parameter value ^a
<i>Na</i>	0.001		<i>Na</i>	0.0006
<i>Mg</i>	0.8		<i>Mg</i>	0.969
<i>Ca</i>	0.028		<i>Ca</i>	0.031
<i>Fe</i>	0.003		<i>Fe</i>	0.001
<i>Al</i>	0.00002		<i>Al</i>	0.00002
<i>Si</i>	0.003		<i>Si</i>	0.002
<i>Cl</i>	0.001		<i>Cl</i>	0.0006
<i>C</i>	0.05		<i>C</i>	2.413
<i>CH_{4,aq}</i>	0.0314		<i>CH_{4,aq}</i>	2.408
<i>HCO₃⁻</i>	0.0038		<i>HCO₃⁻</i>	9e-7
<i>Ca(HCO₃)⁺</i>	0.0067		<i>Ca(HCO₃)⁺</i>	2e-6
<i>CO₃²⁻</i>	0.0002		<i>CO₃²⁻</i>	6e-8
<i>CaCO_{3,aq}</i>	0.0013		<i>CaCO_{3,aq}</i>	6e-7
<i>H₂CO_{3,aq}</i>	0.0003		<i>H₂CO_{3,aq}</i>	6e-8
<i>CO_{2,aq}</i>	0.0004		<i>CO_{2,aq}</i>	8e-8
<i>HCOO⁻</i>	0.0011		<i>HCOO⁻</i>	7e-6
<i>Fe(HCOO)⁺</i>	0.0024		<i>Fe(HCOO)⁺</i>	0.00005
<i>Ca(HCOO)⁺</i>	0.0016		<i>Ca(HCOO)⁺</i>	0.00001
<i>pH</i>	5.64		<i>pH</i>	5.77
Neutral <i>pH</i>	3.60		Neutral <i>pH</i>	3.60
<i>logf_{O₂}</i>	-27.4		<i>logf_{O₂}</i>	-30.2
ΔQFM	-1.3		ΔQFM	-4.1
REACTANT MINERALS	COMPONENTS	REACTANT MOLE FRACTION	FINAL PRODUCT MOLE FRACTION	FINAL PRODUCT MOLES
ARAGONITE	<i>CaCO₃</i>	1.0	n.d.	0.0
ANTIGORITE	<i>Mg₂₄Si₁₇O_{73.5}H₃₁</i>	1.0	1.0	1.598
MAGNETITE	<i>Fe₃O₄</i>	1.0	1.0	0.113
CHLORITE	Clinocllore	0.97	0.90	1.696
	Chamosite	0.03	0.10	0.188
PRODUCT MINERALS	COMPONENTS			
CLINOPYROXENE	Diopside	n.d.	0.90	14.786
	Hedenbergite	n.d.	0.10	1.643
	Jadeite	n.d.	0.0	0.0
BRUCITE	<i>Mg(OH)₂</i>	n.d.	1.0	31.053
GRAPHITE	<i>C</i>	n.d.	n.d.	0.0

4 ^a Concentrations given in molality (m).

5 **Table 2.** The amounts of initial reactant H_2 , and the initial and final rock and fluid-rock (F/R)
 6 mass ratios, as well as the final excess of H_2O created and the amounts of immiscible hydrocarbon
 7 fluid created.

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Reactants				Final			
F/R	M_R^a	$N_{H_2}^b$	H_2/R^c	$M_R'^a$	F/R'	Extra $N_{H_2O}^d$	N_{HC}^e
0.10	10.0	66.5	0.0133	9.27	0.17	32.3	12.7
0.20	5.00	33.2	0.0133	4.63	0.28	16.5	5.15
0.33	3.03	20.2	0.0133	2.81	0.42	10.3	2.20
0.63	1.59	10.6	0.0133	1.46	0.75	5.57	0.012

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10 ^a mass of rock in kg, ^b moles of H_2 , ^c mass ratio of H_2 and rock, ^dExcess moles of water created
 11 relative to the initial 55.51 moles, ^e moles of hydrocarbon fluid created.

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16 **Table 3.** The final hydrogen budget (mole of element percentage) of the model at 2.0 GPa &
 17 400 °C with F/R 0.1.

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Mineral		Aqueous fluid		Hydrocarbon fluid	
antigorite	14.1%	$CH_{4,aq}$	4.2%	$CH_{4,f}$	14.4%
brucite	17.7%	H_2O	49.6%		
chlorite	<1%	$Mg(OH)_2$	<1%		

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