Ongoing alteration of mantle peridotite in the weathering horizon: Initial results from the Oman Drilling Project Multi-Borehole Observatory

Peter B Kelemen¹, James A Leong², Juan Carlos de Obeso³, Juerg Matter⁴, Eric T Ellison⁵, Alexis S Templeton⁶, Daniel B Nothaft⁷, Alireza Eslami⁸, Katy Evans⁹, Marguerite Godard¹⁰, Jude A Coggon¹¹, Nehal H. Warsi¹², Philippe Pézard¹³, Saebyul Choe¹⁴, Damon Teagle¹⁵, Katsuyoshi Michibayashi¹⁶, Eiichi Takazawa¹⁷, and Zaher Al Sulaimani¹⁸

¹Columbia University ²LDEO, Columbia University ³University of Calgary ⁴University of Southampton ⁵University of Colorado ⁶University of Colorado Boulder ⁷University of Pennsylvania ⁸ISTerre, Université Grenoble Alpes ⁹Curtin University of Technology ¹⁰Universite de Montpellier ¹¹School of Ocean & Earth Science, University of Southampton ¹²Alara Resources Ltd. ¹³CNRS Géosciences, Université de Montpellier ¹⁴Dept. of Earth & Planetary Sciences, American Museum of Natural History ¹⁵National Oceanography Centre Southampton ¹⁶Nagoya University ¹⁷Niigata University ¹⁸Oman Water Society

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Abstract

The Oman Drilling Project "Multi-Borehole Observatory" (MBO) samples an area of active weathering of tectonically exposed peridotite. This paper reviews the geology of the MBO region, summarizes recent research, and provides new data constraining ongoing alteration. Host rocks are partially to completely serpentinized, residual mantle harzburgites and replacive. Dunites show evidence for "reactive fractionation", in which cooling, crystallizing magmas reacted with older residues of melting. Harzburgites and dunites are 65-100% hydrated. Ferric to total iron ratios vary from 50 to 90%. In Hole BA1B, alteration extent decreases with depth. Gradients in water and core composition are correlated. Serpentine veins are intergrown with, and cut, carbonate veins with measurable ¹⁴C. Ongoing hydration is accompanied by SiO₂ addition. Sulfur enrichment in Hole BA1B may result from oxidative leaching of sulfur from the upper 30 m, coupled with sulfate reduction and sulfide precipitation at 30-150 m. Oxygen fugacity deep in Holes BA3A, NSHQ14 and BA2A is fixed by the reaction $2H_2O = 2H_2 + O_2$ combined with oxidation of ferrous iron in serpentine, brucite and olivine. fO₂ deep in Holes BA1A, BA1D and BA4A is 3-4 log units above the H_2O-H_2 limit, controlled by equilibria involving serpentine and brucite. Variations in alteration are correlated with texture, with reduced, low SiO₂ assemblages in mesh cores recording very low water/rock ratios, juxtaposed with adjacent veins recording much higher ratios. The proportion of reduced mesh cores vs oxidized veins increases with depth, and the difference in fO₂ recorded in cores and veins decreases with depth.

COLUMBIA UNIVERSITY

IN THE CITY OF NEW YORK DEPARTMENT OF EARTH & ENVIRONMENTAL SCIENCES LAMONT DOHERTY EARTH OBSERVATORY

Prof. Stephen Parman Editor, JGR Solid Earth June 30, 2021

Dear Steve,

With this letter, my co-authors and I are submitting a multi-authored paper, "Ongoing alteration of mantle peridotite in the weathering horizon: Initial results from the Oman Drilling Project Multi-Borehole Observatory". If this paper is accepted, we are requesting that it be included in the Special Issue on Ophiolites and Oceanic Lithosphere.

This paper cites five papers that are in revision or review at JGR. In the bibliography of this paper, all five references are highlighted in red font, and links are provided to preprints archived at ESSOAr. In view of the fact that this paper is an overview of collaborative research involving many scientists, and is submitted to a Special Issue where these papers will be collected. I hope that you will find this acceptable. There are several more papers submitted to the JGR Special Issue, or about to be submitted, that are not currently available at ESSOAr. In the hope of streamlining this submission process. I have deleted reference to those papers.

We are suggesting that you handle this paper since you – as a petrologist – have a broad knowledge of the potential reviewing community and scientific issues.

We would like to recommend the following potential reviewers:

Wolfgang Bach <u>wbach@uni-bremen.de</u> Jim Beard <u>jim.beard@wnnh.virginia.gov</u> Ron Frost <u>RFrost@wwoo.edu</u> Frieder Klein <u>fklein@whoi.edu</u> Esther Schwarzenbach <u>esther.schwarzenbach@fu-berlin.de</u> Bill Seyfried <u>wes@umn.edu</u> Ben Tutolo <u>benjamin.tutolo@ucalgary.ca</u>

With so much current interest in serpentinization, it is easy to pick potential reviewers!

Based on some not-so-friendly, recent email correspondence, we request that the paper not be sent for review to Everett Shock. We will share a copy of this manuscript with him informally, seeking his input.

Thank you in advance for your consideration of our paper.

On behalf of myself and seventeen co-authors, sincerely,

Kon B Ku

Peter B. Kelemen Arthur D. Storke Professor Dept. of Earth & Environmental Sciences peterk@LDEO.columbia.edu

Lamont Doherty Earth Observatory 211 Comer Laboratory P.O. Box 1000 61 Route 9W Palisades, NY 10964-8000 USA Columbia University 557 Schermerhorn Extension Mail Code 5505 New York, NY 10027 USA http://eesc.columbia.edu/

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1: Lamont Doherty Earth Observatory, Columbia University, Palisades NY 10964, peterk@LDEO.columbia.edu ... 2. Dept. of Geosciences, University of Calgary 3. School of Ocean & Earth Science, University of Southampton 4. Dept. of Geological Sciences, University of Colorado, Boulder 5. School of Engineering and Applied Sciences, University of Pennsylvania 6: ISTerre, Université de Grenoble-Alps 7: School of Earth & Planetary Sci., Curtin University 8: CNRS Géosciences, Université de Montpellier 9. Alara Resources Ltd., Oman 10. Dept. of Earth & Planetary Sci., American Museum of Natural History ... 11. Dept. of Earth & Planetary Sciences, Nagoya University 12. Dept. of Geology, Niigata University & VERC IMG JAMSTEC 13. Oman Water Society & Middle East Desalination Research Center

Abstract

19 The Oman Drilling Project "Multi-Borehole Observatory" (MBO) samples an area of active weathering 20 of tectonically exposed peridotite. This paper reviews the geology of the MBO region, summarizes recent research, and provides new data constraining ongoing alteration. Host rocks are partially to 21 22 completely serpentinized, residual mantle harzburgites and replacive. Dunites show evidence for "reactive fractionation", in which cooling, crystallizing magmas reacted with older residues of melting. 23 Harzburgites and dunites are 65-100% hydrated. Ferric to total iron ratios vary from 50 to 90%. In 24 Hole BA1B, alteration extent decreases with depth. Gradients in water and core composition are 25 26 correlated. Serpentine veins are intergrown with, and cut, carbonate veins with measurable ¹⁴C. 27 Ongoing hydration is accompanied by SiO₂ addition. Sulfur enrichment in Hole BA1B may result from 28 oxidative leaching of sulfur from the upper 30 m, coupled with sulfate reduction and sulfide 29 precipitation at 30-150 m. Oxygen fugacity deep in Holes BA3A, NSHQ14 and BA2A is fixed by the reaction $2H_2O = 2H_2 + O_2$ combined with oxidation of ferrous iron in serpentine, brucite and olivine. 30 fO₂ deep in Holes BA1A, BA1D and BA4A is 3-4 log units above the H₂O-H₂ limit, controlled by 31 equilibria involving serpentine and brucite. Variations in alteration are correlated with texture, with 32 reduced, low SiO₂ assemblages in mesh cores recording very low water/rock ratios, juxtaposed with 33 adjacent veins recording much higher ratios. The proportion of reduced mesh cores vs oxidized veins 34 35 increases with depth, and the difference in fO_2 recorded in cores and veins decreases with depth. 36

Plain Language Summary

38 39 The Oman Drilling Project developed a "Multi-Borehole Observatory" (MBO) in an area of active weathering of tectonically exposed peridotite, to study the geochemistry, mechanics and hydrology of 40 peridotite alteration, which modifies the mineralogy, composition, density and rheology of mantle 41 42 lithologies, creates and sustains plate boundaries, and forms dramatic redox gradients. In turn, these 43 redox conditions support a unique subsurface microbial ecosystem, form free H₂ gas, facilitate methane generation, and potentially play a role in the origin of life on this and other planets. This 44 45 paper provides an overview of the geology of the area within and surrounding the MBO, a summary of 46 recent research on core and fluids from three new cored boreholes and four new rotary boreholes in 47 the MBO, together with older Omani water monitoring well NSHQ14, and new data and calculations constraining ongoing peridotite alteration in this area. We constrain the igneous history of the mantle 48 49 rocks, the extent to which they have been hydrated, carbonated and oxidized. Highlights include new hypotheses on mechanisms of shallow sulfur depletion and deeper enrichment, and new insights into 50 the interaction of water and minerals that controls the partial pressures of oxygen and hydrogen in this 51 important geochemical environment. 52

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1. Introduction

57 The Oman Drilling Project (OmanDP) Multi-Borehole Observatory (MBO) lies in the area bounded by latitudes 22.84 to 22.98°N, and 58.58° to 58.76°E (Figures 1, 2 and 3), northeast of the city of Ibra in 58 the Sultanate of Oman, and close to the town of Batin. This area was chosen for drilling to investigate 59 ongoing hydration, carbonation and oxidation of exposed mantle peridotite during near-surface 60 weathering, the associated hydrological system, and the subsurface, chemosynthetic biosphere 61 fostered by weathering of mantle peridotite. Cores collected in the MBO will also be relevant for 62 understanding mantle melt transport, and quantifying the cooling history of the shallow mantle near a 63 spreading ridge. Conversely, cores from the crust-mantle transition zone (MTZ) drill sites CM1A and 64 65 CM2B in the Wadi Tayin massif, obtained mainly to study near-spreading-ridge igneous, alteration and cooling processes, will shed further light on weathering and the subsurface biosphere in 66 67 tectonically exposed peridotite.

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Figure 1: Outcrop area of the Samail ophiolite in Oman and the United Arab Emirates, based on Nicolas et al. [2000b]. Red rectangles indicate the approximate location of Figure 2, providing place names used in this paper, and Figure 3, a geologic map of the area that is the focus of this paper. Map coordinates are meters in UTM (Universal Transverse Mercator) Zone 40Q.

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Initially, we hoped to conduct drilling of actively altering peridotite in Wadi Dima, west of the present sites, in an area without large faults. However, we were not able to find drill sites more than 3.5 km from the nearest registered "falaj" (irrigation system), as required for permitting. Alternatives were (a) Wadi Laywani, a broad, south-facing drainage about 20 km northeast Batin, and 4 km east of the road from Batin to the village of Dima, and (b) the headwaters of Wadi Mehlah, along the Batin-Dima road. Wadi Mehlah is a long, straight NNW trending valley NNW of Wadi Laywani, parallel to the Batin-Dima road, draining into Wadi Tayin east of Wadi Dima, near its intersection with Wadi Tayin.

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Both of these alternative areas lie along a major NW-SE trending fault system that cuts the Samail
ophiolite (Figure 4). An advantage of Wadi Laywani is that there had been prior sampling and analysis
of water and rock chips from water monitoring wells NSHQ14, NSHQ04, WAB71 and WAB188 in and
near that catchment [*Miller et al.*, 2016; *Paukert et al.*, 2012; *Paukert Vankeuren et al.*, 2019; *Rempfert et al.*, 2017]. (The water monitoring wells have been established and maintained by the
Oman Ministry of Regional Municipalities and Water Resources, and its precursor and successor

85 organizations).

Figure 2: Map showing location of places named in this paper, and the locations of OmanDP Holes GT1 and GT2 (crustal gabbros), GT3 (gabbro-sheeted dike transition), and CM1 and CM2 (crust-mantle transition). Solid lines are roads; thick: paved, thin: gravel. Grey dashed line illustrates the approximate trace of the crust-mantle transition zone in the Wadi Tayin massif of the Samail ophiolite. Red rectangle indicates approximate location of Figure 3.



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OmanDP drilling in the MBO area began with reconnaissance, rotary boreholes in each of the two alternative areas in winter 2017. Hole BA1A is in Wadi Laywani. The water table was encountered at a depth of ~ 16 meters. Drill chips indicated that the bedrock was a mix of serpentinized dunite and harzburgite. Hole BA2A is in the headwaters of Wadi Mehlah. Surrounding outcrops and drill chips indicated that the Hole is almost entirely in dunite. Other than the drilling fluid, there was essentially no water in Hole BA2A within its full depth of 400 meters. As a result, in order to ensure the presence of water for lubrication during coring, we decided to drill all subsequent MBO holes in Wadi Laywani.

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The MBO includes OmanDP Holes BA1A, BA1B, BA1C, BA1D, BA2A, BA3A and BA4A, (The two 97 letter BA designation in the OmanDP Hole names referred to the location, near Batin, and the focus 98 on Alteration). In addition, we have benefited from access to pre-existing Oman Water Ministry 99 monitoring holes NSHQ04, NSHQ14, WAB71 and WAB188. Among these Holes, BA1B, BA3A and 100 BA4A recovered core via wireline diamond drilling (~ 100% recovery), while cuttings from rotary 101 102 boreholes BA1A and BA2A were examined by the OmanDP Science Team, and two groups have also 103 studied cuttings and drilling logs from NSHQ14 [Miller et al., 2016; Paukert et al., 2012]. Core was 104 shipped to Japan and loaded onto Drilling Vessel Chikyu, where the OmanDP Science Team performed analyses closely following protocols established by the various incarnations of the Ocean 105 Drilling Program (formerly the Ocean Drilling Program, ODP, and the International Ocean Drilling 106 Program, IODP; currently, the International Ocean Discovery Program, IODP). Detailed core

Program, IODP; currently, the International Ocean Discovery Program, IODP). Detailed core
 descriptions, together with drilling history and some background information [*Kelemen et al.*, 2021b; c;

- d; e; f; g; *Kelemen et al.*, 2020g] are available online at
- 110 http://publications.iodp.org/other/Oman/VOLUME/CHAPTERS/113 BT1.PDF
- 111 112







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117 Figure 4: Regional scale fault traces transecting the MBO. Wadi Tayin massif mantle peridotites are dark olive green to brown. Gabbros south of the peridotite are greenish grey. The Saih Hatat dome, exposing Proterozoic to 118 Paleozoic shelf sediments, is the grey area northeast of the Wadi Tayin peridotites. Late Cretaceous to Eocene, 119 shallow marine limestones unconformably overlying all of these units on the east, plus smaller erosional 120 121 remnants near the center of the image, are tan. Approximate locations of OmanDP Holes GT3A, CM1&2, GT1, GT2, BA2A, BA4A, BA1A-D, and BA3A (plus pre-existing water monitoring well NSHQ14 adjacent to BA3A), 122 listed in order from W to E, are shown as large vellow circles. Approximate locations of other, pre-existing water 123 124 monitoring wells within the MBO are shown as smaller yellow circles. Yellow versus red colors for inferred fault 125 traces were used simply for visibility. 126

1.1 Regional geology and structure of the MBO and vicinity

The MBO Holes are entirely within partially to completely serpentinized peridotite comprising the mantle section of Wadi Tayin massif of the Samail ophiolite. Peridotites in the Wadi Tayin and nearbyt Samail massif mantle sections record at least one phase of extensive melting and melt-extraction, producing residual harzburgites. The harzburgites record ~ 15 to 20% melt extraction, assuming the protolith had a fertile lherzolite composition and have major and trace element contents very similar to residual mantle peridotites dredged from mid-ocean ridges [*M Godard et al.*, 2000; *Hanghøj et al.*, 2010; *Kelemen et al.*, 1997a; *Kelemen et al.*, 1995a; *Monnier et al.*, 2006].

136 In the northern massifs of the ophiolite, there are clear indications that two important stages of partial 137 melting and melt transport affected the mantle section, one during upwelling and corner flow in the 138 139 shallow mantle beneath an oceanic spreading ridge, and a later one producing cross-cutting features. 140 Products of the second stage are relatively rare in the southern massifs of the ophiolite, including 141 Wadi Tayin and the neighboring Samail massif. For example, one characteristic of peridotites strongly 142 affected by the second stage is high Cr# (molar Cr/(Cr+Al)) in spinels, ranging from 0.7 to 0.9 [e.g., 143 Arai et al., 2006; Tamura and Arai, 2006, and references therein]. Such high Cr# is generally taken to 144 indicate the effects of arc magmatism. In contrast, spinels in the southern massifs of the Samail ophiolite show a broad range of more aluminous compositions, with Cr# from ~ 0.2 to 0.73 [e.g., M 145

146 Godard et al., 2000; Hanghøj et al., 2010; Kelemen et al., 1997a; Kelemen et al., 1995a; Monnier et

147 al., 2006], similar to the range in peridotites dredged from the mid-ocean ridges [~ 0.1 to 0.69, H Dick 148 and Bullen, 1984; El Dien et al., 2019; Urann et al., 2020]. We don't want to be misunderstood here; the Samail ophiolite lavas, from southern as well as northern massifs, contain a distinct geochemical 149 subduction signature [e.g., Alabaster et al., 1982; MacLeod et al., 2013; Pearce et al., 1981; Pearce 150 and Peate, 1995]. Conversely, the samples with highest Cr# spinels dredged from the Mid-Atlantic 151 152 Ridge have been attributed to the presence of a fragment of depleted arc lithosphere beneath the ridge [Urann et al., 2020]. However, there is little evidence for a profound difference in melt generation 153 and extraction processes, when comparing mid-ocean ridge peridotites with Samail ophiolite 154 peridotites from the southern, Wadi Tayin and Samail massifs in Oman. 155

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The Wadi Tayin massif is one of the largest and most intact massifs in the ophiolite. A well-exposed 157 158 crustal section in the "Ibra syncline", about 7 km thick from seafloor pillow lavas to the mantle-crust transition zone (MTZ), has been the subject of many detailed studies [e.g., papers in Bieseler et al., 159 2018; Bosch et al., 2004; Boudier et al., 1996; Coleman and Hopson, 1981; Coogan et al., 2006; 160 Currin et al., 2018; France et al., 2009; Garrido et al., 2001; Kelemen and Aharonov, 1998; Kelemen 161 162 et al., 1997b; Koga et al., 2001; Korenaga and Kelemen, 1997; Mock et al., 2021; Müller et al., 2017; 163 Nicolas et al., 2003; Oeser et al., 2012; Peucker-Ehrenbrink et al., 2012; Rajendran and Nasir, 2019; Rioux et al., 2012; VanTongeren et al., 2015; VanTongeren et al., 2008; Zihlmann et al., 2018]. 164 OmanDP Holes GT1A and GT2A, drilled in winter 2017, sampled lower crustal gabbros in this 165 section, while Hole GT3A sampled the sheeted-dike to upper gabbro transition in a nearby part of the 166 Samail massif [Kelemen et al., 2020b; d; e; f]. The MTZ of the Wadi Tayin massif is exposed in 167 outcrop in several places, including Wadi Nassif and the smaller, adjacent Wadi Zeeb. The latter was 168 the site of Holes CM1A,B, and CM2A,B in late fall 2017, which provided a complete core sample 169 through the transition zone [Kelemen et al., 2021a; h; i]. The MTZ dips 20 to 30° SSW along the strike 170 171 length of the Wadi Tayin massif [Bailey, 1981; Nicolas et al., 2000b].

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If there has been no tectonic thinning or thickening, then the thickness of the mantle section -173 perpendicular to the MTZ and the paleo-seafloor - ranges from 10 to 20 km below the base of the 174 crust [Boudier and Coleman, 1981], yielding a maximum thickness for the entire Wadi Tayin massif of 175 ~ 25 km. At the base of the mantle section throughout the ophiolite is the trace-element-enriched 176 177 "Banded Unit", composed of 1 to 10 m scale bands of harzburgite, dunite and rare lherzolite, overlying 178 a metamorphic sole composed mainly of amphibolites [M Godard et al., 2000; Khedr et al., 2013; 179 Khedr et al., 2014; Takazawa et al., 2003; Yoshikawa et al., 2015]. Locally, the Wadi Tayin Banded 180 Unit includes mylonitic shear zones, which formed at an inferred temperature of 700-1000°C [Boudier et al., 1988; Boudier and Coleman, 1981]. This sequence is characteristic of the base of the most 181 complete, best-exposed sections throughout the Samail ophiolite, where the underlying metamorphic 182 sole is preserved. The metamorphic sole in Wadi Tayin records peak metamorphism at ~ 700-900°C 183 and ~ 1.2 GPa [e.g., Cowan et al., 2014; Hacker and Mosenfelder, 1996; M Searle and Cox, 2002; M 184 P Searle and Malpas, 1980; Soret et al., 2017], roughly consistent with the thickness estimate and 185 deformation temperature inferred for the base of the Wadi Tayin peridotite section. 186

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The MTZ and surrounding crust and mantle are cut and displaced by several kilometers along a set of 188 NNW trending, strike-slip faults [Bailey, 1981; Nicolas et al., 2000b]. In the MBO area, these have a 189 190 right lateral sense of displacement. Perhaps related to these smaller features, a 10- to 50-km-scale NNW trending fault system evident in satellite imagery cuts all the way across the Wadi Tayin massif 191 in Wadi Laywani (draining south) and Wadi Mehlah (draining north) (Figure 4). The sense of 192 193 displacement along this larger fault system has not been determined, but it is possible that it too is a 194 right-lateral, strike-slip fault.

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Near the western end of the Wadi Tayin massif, a large strike-slip fault shows left lateral displacement 196 of the MTZ along Wadi Khafifah. This continues as a ductile shear zone extending several kilometers 197 into the mantle section [Nicolas and Boudier, 2008]. Along this shear zone, deformation was localized 198 in gabbroic dikes within the mantle [Homburg et al., 2010]. Strongly deformed gabbroic dikes are also 199 observed in outcrop in the MBO region. Ductile deformation of the dikes may be related movement 200 along the large fault system; if so, the faults became active while the mantle section of the Wadi Tayin 201 202 massif was still at high temperature, though deformation has apparently continued into the lowtemperature, brittle regime. 203

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205 Normally, Samail ophiolite peridotites have a foliation that is approximately parallel to the MTZ and the paleo-seafloor [e.g., synoptic cross-sections in Lippard et al., 1986; Nicolas et al., 1988]. A 206

peculiar structural relationship has been observed – but rarely documented in publications – across
central parts of the Wadi Tayin mantle section, in which peridotite foliation – marked by faint,
pyroxene-rich banding – dips steeply with respect to the shallow dip of the MTZ [e.g., *Boudier and Coleman*, 1981, their Figure 2]. Despite this steep foliation, dunite-harzburgite contacts have a low
dip, approximately parallel to that of the MTZ, and spinel lineation within the steeply dipping peridotite
foliation has a low inclination.

Perhaps fortunately, indications from surface mapping and drill site observation of core are that peridotite foliation at the MBO sites has a shallow dip, approximately parallel to the MTZ exposed in east facing outcrops on ridges forming the west side of Wadi Laywani, SW of Site BA3, as illustrated in the widely used, synoptic cross-sections of the Samail ophiolite. Here, we simply mention the odd geometry of foliation and lineation further west in the Wadi Tayin massif, because it may be important in future syntheses of drilling results and surface observations.

1.2 Mantle dunites in the MBO and vicinity

Geological mapping in the late 1970's identified two particularly large dunite bodies in the Wadi Tayin mantle section, within depleted, residual mantle harzburgite [*Bailey*, 1981]. The dunites dip 20 to 30° SSW, approximately parallel to the overlying MTZ. Kelemen et al. [2000, their Table 1] measured the thickness of the northeastern dunite body, perpendicular to top and bottom contacts with harzburgite, to be ~ 70 meters, in the range of other large mantle dunites. More extensive size-frequency data on mantle dunites are reported by Braun & Kelemen [2002].

Unpublished observations by Peter Kelemen, and later by Bob Miller (California State University, San
Jose) confirmed the SSW dip of the southwestern dunite body at its thin, northwestern tip, where it is
about 2 km below the MTZ. However, there have been no estimates of its thickness in its central
region, at Site BA2 for example, due to faulting and irregular contacts.

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Between the two large, SSW dipping dunites is a zone containing of thinner dunites, up to 20 m wide, with steep NNE dips (Figure 3). This NW striking zone is approximately coincident with the Batin – Dima road, and not more than 3 km wide. This zone may be the locus of steeply inclined spinel lineations reported by Nicolas et al. [*Nicolas et al.*, 2000a], who interpreted such steep lineations as indicative of the presence of "mantle diapirs".

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One potential explanation for these relationships - with shallow dunites to the SW and NE, flanking a 241 242 central zone of steeply dipping dunites, is that the central dunites represent a frozen zone of mantle 243 upwelling beneath a spreading center, whereas the MTZ parallel dunites to the NE and SW have been transposed by corner flow on either side of the ridge. However, given that the Wadi Tayin 244 massif, and overlying Late Cretaceous to Eocene limestones, are clearly faulted and tilted within the 245 246 area of the left panel in Figure 3, it is not clear whether features within the mantle section retain their structural orientation, with respect to each other and to the crust-mantle transition zone (MTZ). Thus, 247 248 the narrow zone of steep dunites could be a preserved relict of the upwelling zone in the mantle 249 beneath a spreading center, or the result of post-emplacement, tectonic rotations within the Wadi 250 Tayin massif. 251

As is evident from geologic mapping, Sites BA2 and BA4 lie within the outcrop of the southeastern tip 252 253 of the large, shallowly SSW dipping dunite body, and most Holes in Site BA1 - in gravels within Wadi Laywani – also intersect that large dunite (Figure 5). On site observations of drill cuttings [Kelemen et 254 al., 2021e] indicate that the entire 400 meter Hole BA2A is within massive dunite. Assuming a SW dip 255 of 25 to 30 degrees parallel to the MTZ, this indicates that the dunite at Site BA2A is more than 350 256 meters thick, perpendicular to the MTZ. As such, it is more than three times thicker than the next 257 258 thickest dunite in the mantle section of the Samail ophiolite, as measured by Kelemen et al. [2000, 259 their Table 1].

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Core from Hole BA4A, and surrounding outcrops, are composed of alternating bands of dunite and harzburgite [*Kelemen et al.*, 2021g], rather than the more massive dunites in outcrop further to the NW. However, to the SE, Holes BA1A, B, C and D again intersected the large dunite body, where it is massive, containing only a few thin harzburgite lenses, ~ 100-200 m thick, and about 2 km structurally beneath the MTZ [*Kelemen et al.*, 2021d]. The upper 150 meters of core from Hole BA1B was largely composed of dunite, with relatively few harzburgite bands. The large dunite may or may not extend 267 across Wadi Laywani. Approximate logs based on drill cuttings suggest that the top of Hole BA1C 268 intersected ~ 100 m of dunite near the east side of the Wadi, and a few relatively thin, SSW dipping dunite lenses can be seen on WSW facing-outcrops flanking the Wadi to the east (Figure 3). If the 269 overall, thick dunite unit does cross the Wadi, this places an upper bound of a few hundred meters on 270 displacement along the fault zone(s) within Wadi Laywani. 271



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275 Figure 5: Lithologic columns based on analysis of drill core from Holes BA1B. BA3A and BA4A, and drill cuttings 276 from Holes BA1A, BA1C, BA1D and BA2A, from Kelemen et al. [2021d; e; f; g]. 277

278 Dunites in the mantle section of ophiolites – and by inference in the mantle beneath oceanic 279 spreading ridges - are generally understood to be the products of reaction between olivine-saturated 280 melt – ascending by porous flow along crystal grain boundaries – and shallow mantle harzburgites. 281 Orthopyroxene from the harzburgite dissolves, producing olivine + melt, and this leads to formation of 282 dunites in channels of focused porous flow [e.g., Aharonov et al., 1995; J L Bodinier, 1988; Kelemen, 1990; Kelemen et al., 1995a; Kelemen et al., 1995b; Quick, 1982]. Typically, unless modified by 283 subsolidus, low temperature Fe/Mg exchange with spinel, olivine in mantle dunites has about the 284 same composition (Mg#, molar Mg/(Mg+Fe), ~ 0.91) as in the surrounding harzburgites [Kelemen, 285 1990], consistent with formation of dunite by reaction, rather than as the residue of extensive partial 286 melting and melt extraction [e.g., as advocated by Benoit et al., 1999; Rospabé et al., 2017], or as 287 288 newly crystallized magmatic rocks ["cumulate dunites", e.g., Rollinson, 2019]. 289

As melt approaches the surface and begins to cool, it will begin to undergo crystallization and 290 accompanying chemical fractionation, potentially producing olivine with a lower Mg#. If it continues to 291 react with mantle peridotite, open system processes will buffer the composition of cooling melt to 292 various degrees, in a process termed "reactive fractionation" [Abily and Ceuleneer, 2013; Collier and 293 294 Kelemen, 2010]. This process can produce trends typical of reaction between fractionating melt and 295 mantle peridotite with increasing incompatible element concentrations at nearly constant compatible element concentrations [e.g., Kelemen, 1986; 1990]. Using major elements alone, diagnostic 296 characteristics of dunites and "troctolites" (plagioclase bearing dunites and impregnated peridotites) 297 produced by reactive fractionation are nearly constant Ni content over a range of Mg#, together with a 298 299 wide range of Ca# (molar Ca/(Ca+Na), also known as normative anorthite content), as emphasized in several studies of "impregnated dunites" and "troctolites" recovered via dredging and drilling along the 300 mid-ocean ridges, and outcrop sampling in ophiolites [Arai and Matsukage, 1996; Basch et al., 2018; 301 2019; Brunelli et al., 2006; Collier and Kelemen, 2010; H J Dick and Natland, 1996; Drouin et al., 302 2009; Drouin et al., 2010; Ferrando et al., 2018; Gillis et al., 2014; M. Godard et al., 2009; Kelemen et 303 al., 2004; Kelemen et al., 2007; Seyler and Bonatti, 1997; Seyler et al., 2007; Suhr et al., 2008; 304 Takazawa et al., 2007; Tartarotti et al., 2002]. 305

1.3 Mantle dikes in the MBO and vicinity

Cutting the dunite around the MBO sites are numerous, tabular gabbroic and pyroxenite dikes. 308 Though this has not yet been quantified, it is qualitatively evident that the dikes are more numerous 309 than is typical in the mantle section of the Samail ophiolite. The dikes range from fine-grained to 310 311 pegmatoidal, and may be an important source of calcium and, locally, aluminum during alteration and weathering of the peridotite. It is not clear why there is an unusual number of dikes in the vicinity of 312 the MBO. However, the presence of dikes in the mantle section of the Samail ophiolite is common. A 313 late set of gabbronorite and websterite dikes cutting mantle peridotite foliation and dunite contacts 314 occurs throughout the ophiolite [Benoit et al., 1999; Benoit et al., 1996; Ceuleneer et al., 1996; 315 Kelemen et al., 1997a; Python and Ceuleneer, 2003]. Geochemical characteristics of these dikes 316 317 indicate that they are not related to the magmas that formed the overlying crust, and could be formed from small amounts of late, shallow melts of residual mantle harzburgite [Kelemen et al., 1997a]. They 318 could be related to large websterite and gabbronorite intrusions into the mantle and crust in the 319 northern massifs of the ophiolite [summary in Python and Ceuleneer, 2003; Smewing, 1981]. Less 320 321 commonly (but not far away, in the Samail massif of the ophiolite), there are also olivine gabbro and 322 troctolite dikes in the mantle, which could have crystallized from the same kind of magmas that 323 formed most of the crust [Ceuleneer et al., 1996; Python and Ceuleneer, 2003]. Because the dikes in the MBO area have been substantially altered to calc-silicate, "rodingite" assemblages during 324 325 serpentinization, it is not yet clear which kinds of lithologies predominate in the dike swarm around the BA sites. 326

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1.4 Post-emplacement alteration of the MBO and vicinity

329 330 Emplacement of the ophiolite, and the underlying, allochthonous Hawasina Formation, onto the 331 Arabian continental margin, followed by subaerial weathering of the ophiolite, was complete by about 332 74 Ma, based on the age of the oldest sediments overlying an erosional unconformity at the top of the ophiolite section [S Al Khirbash, 2015; Alsharan and Nasir, 1996; Bailey, 1981; Hansman et al., 2017; 333 Nolan et al., 1990; Schlüter et al., 2008; Wyns et al., 1992]. Extensive erosion of the eastern part of 334 335 the Wadi Tayin massif exposed mantle peridotite at the surface, locally forming laterites in a 336 discontinuous band that extends to ~ 3 km E of Sites BA1, 3 and 4 [S Al Khirbash, 2015; S A Al 337 Khirbash, 2016; 2020], and well exposed erosional surfaces overlain by peridotite conglomerates in 338 erosional windows near the coast east and northeast of Wadi Tayin [de Obeso and Kelemen, 2018; 2020]. After marine transpression. Late Cretaceous and Tertiary shallow water sediments were 339 deposited unconformably on the peridotites in this area [Alsharan and Nasir, 1996; Hansman et al., 340 2017; Nolan et al., 1990]. As a result of this history, without careful study, it is not immediately clear 341 342 how much of the low temperature alteration of the peridotite in the MBO, and in the Wadi Tayin massif more generally, may have occurred in the Late Cretaceous, and how much is related to more recent, 343 ongoing weathering. Noël et al. [Noël et al., 2018] propose that the stable isotope characteristics of 344 some serpentinites record "high" alteration temperatures consistent with early alteration near the axis 345 of the spreading ridge that formed the ophiolite crust, and/or during early stages of ophiolite 346 347 emplacement. However, we regard this result as uncertain, because their inferred alteration temperatures (~ 115-10°C) are lower than the temperature in the shallow mantle beneath oceanic 348 349 crust (~100°C at the Moho in ocean crust > 60 million years old, hotter in younger crust) and temperatures at the base of the crust during metamorphism of the metamorphic sole (800-900°C at ~ 350 40 km, so more than 140°C at 7 km). 351

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Turning attention from the MBO region to the Samail ophiolite in general, studies of low temperature 353 peridotite alteration in the mantle section of the Samail ophiolite have been more limited than studies 354 of mantle melting and melt transport, and studies of oceanic crustal formation and alteration. Early 355 work by Barnes et al. [1978] and Neal, Stanger and their colleagues [Neal and Stanger, 1983; 1984; 356 1985; Stanger and Neal, 1994] focused on the production of hyperalkaline spring water and H₂-rich 357 358 gas during peridotite weathering, further refining the insights of Barnes and O'Neil [1969] that were based on observations of similar systems in California. Stanger and colleagues also wrote papers 359 about unusual minerals formed in low temperature weathering of peridotite in Oman [Stanger et al., 360 1988; Stanger and Neal, 1994; Taylor et al., 1991]. Boudier and colleagues investigated seismic 361 anisotropy in partially serpentinized peridotites from Oman and other regions [Boudier et al., 2010; 362 Dewandel et al., 2003]. Clark and Fontes and co-workers investigated travertine deposits forming at 363 364 peridotite-hosted, alkaline springs [1990]. 365

366 Three relatively recent developments led to increased interest in specific aspects low temperature 367 alteration of peridotite, in the Samail ophiolite and worldwide. First, there has been widespread recognition that highly reducing environments and large redox gradients produced during 368 serpentinization [e.g., Frost, 1985] can stabilize hydrocarbons and provide energy for microbial 369 chemosynthesis, leading to an explosion of hypotheses concerning the subsurface biosphere, abiotic 370 371 hydrocarbon genesis, and the origin of life on this and other planets [e.g., Berndt et al., 1996; Ehlmann et al., 2010; Ehlmann et al., 2009; Etiope et al., 2013; Fisk and Giovannoni, 1999; 372 Foustoukos and Seyfried, 2004; Frost and Beard, 2007; Horita and Berndt, 1999; Martin et al., 2008; 373 Martin and Russell, 2007; McCollom, 1999; 2007; Russell et al., 2010; Schulte et al., 2006; Shock, 374 1997; Shock et al., 1995; Sleep et al., 2011; Sleep et al., 2004; Varnes et al., 2003]. There has been a 375 substantial amount of work on the Samail ophiolite related to this topic [Boyd et al., 2020; Canovas et 376 377 al., 2017; de Obeso and Kelemen, 2018; 2020; Ellison et al., 2021; Fones et al., 2019; Fones et al., 378 2021; Glombitza et al., 2021; Kraus et al., 2021; J A Leong et al., 2021a; J A M Leong et al., 2021b; J A M Leong and Shock, 2020; L.E. Mayhew et al., 2018; Miller et al., 2016; Newman et al., 2020; 379 Nothaft et al., 2021a; Nothaft et al., 2021b; Rempfert et al., 2017; Sano et al., 1993Boulart, 2013 380 381 #633; A Templeton et al., 2021; Vacquand et al., 2018].

382 Second, it has been proposed that formation of carbonate minerals via reaction of surface waters with 383 peridotite can produce a significant carbon reservoir on this and other planets, and could potentially 384 be emulated in accelerated systems for engineered carbon capture and storage [e.g., Kelemen and 385 Matter, 2008]. There have been numerous, related studies of carbon mineralization during natural 386 weathering of peridotite in the Samail ophiolite [Chavagnac et al., 2013a; Chavagnac et al., 2013b; 387 Falk et al., 2016; Giampouras et al., 2020; Kelemen et al., 2011; Lacinska and Styles, 2013; Lacinska 388 et al., 2014; Leleu et al., 2016; Mervine et al., 2014; Mervine et al., 2015; Noël et al., 2018; Paukert et 389 390 al., 2012; Paukert Vankeuren et al., 2019; Rajendran and Nasir, 2019; Rajendran et al., 2014; Streit et 391 al., 2012], elsewhere on Earth [e.g., Alt et al., 2013; Alt et al., 2012; Andrews et al., 2018; Arcilla et al., 2011; Beinlich et al., 2010; del Real et al., 2016; Gahlan et al., 2020; Manuella et al., 2019; Morrissey 392 393 and Morrill, 2017; Oskierski et al., 2013a; Oskierski et al., 2013b; c; Picazo et al., 2020; Benoit Quesnel et al., 2016; Benoît Quesnel et al., 2013; Sánchez-Murillo et al., 2014; Schwarzenbach et al., 394 395 2016; Schwarzenbach et al., 2013; Ulrich et al., 2014], and on Mars [e.g., Edwards and Ehlmann, 396 2015; Ehlmann and Edwards, 2014; Ehlmann et al., 2008; Kelemen et al., 2020a; Salvatore et al., 397 2018; Tarnas et al., 2021; Tomkinson et al., 2013]. References listed here are in addition to studies of carbon mineralization - forming completely carbonated "listvenites" - at the base of the Samail 398 ophiolite mantle section and elsewhere on Earth, summarized in a companion paper to this one 399 [Kelemen et al., 2021j] on OmanDP Hole BT1B, which sampled Cretaceous listvenites at the "leading 400 401 edge of the mantle wedge", which formed just above the basal thrust of the ophiolite during subduction and obduction of carbon-bearing sediments 402

403 Third, there has been renewed focus on the volume changes associated with hydration, carbonation 404 and oxidation of peridotite during weathering, as originally addressed by MacDonald and Fyfe [1985], 405 O'Hanley [1992] and Evans [2004], and on the ways in which these volume changes may be 406 accommodated [O Evans et al., 2018; 2020; lyer et al., 2008; Jamtveit et al., 2009; Kelemen and 407 408 Hirth, 2012; Klein and Le Roux, 2020; H Lisabeth et al., 2017a; H P Lisabeth et al., 2017b; Malvoisin 409 et al., 2017; Røyne and Jamtveit, 2015; Rudge et al., 2010; Ulven et al., 2014a; Ulven et al., 2014b; Zheng et al., 2019; Zheng et al., 2018; Zhu et al., 2016]. Studies addressing this issue via study of low 410 411 temperature peridotite weathering in the Samail ophiolite include Kelemen and Hirth [2012], Malvoisin 412 et al. [Malvoisin et al., 2020] and Yoshida et al. [2020]. More generally, fracture-related frequency, porosity and permeability in serpentinized peridotites has been studied in OmanDP drill core samples 413 414 by Katayama et al. [2020; 2021]. 415

In general, it has been noted that Samail ophiolite mantle peridotite compositions are slightly displaced toward lower Mg/Si compared to inferred and experimentally observed residues of partial melting, and the composition of residual peridotites dredged from mid-ocean ridges [e.g., *Monnier et al.*, 2006, their Figure 5]. This is most evident where peridotites are strongly weathered, and could be due to magnesium extraction [*Snow and Dick*, 1995], silicon addition [e.g., *de Obeso and Kelemen*, 2018] or both. Similarly, Mg/Si in drill core from the MBO is low compared to the residues of partial melting and melt as illustrated and discussed in <u>Section 4.3</u>.

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1.5 Past studies of groundwater composition and hydrology in the MBO and vicinity

Groundwater composition and hydrology in the mantle section of the Samail ophiolite has been a 428 subject of fairly extensive research [Canovas et al., 2017; Chavagnac et al., 2013a; Chavagnac et al., 429 2013b; Dewandel et al., 2005; Dewandel et al., 2004; Falk et al., 2016; Leleu et al., 2016; J A M 430 431 Leong et al., 2021b; J A M Leong and Shock, 2020; Lods et al., 2020; Mervine et al., 2014; Mervine et al., 2015; Miller et al., 2016; Monnin et al., 2014; Neal and Stanger, 1985; Noël et al., 2018; Nothaft et 432 al., 2021a; Nothaft et al., 2021b; Paukert et al., 2012; Rempfert et al., 2017]. As described in a classic 433 paper about peridotite-hosted springs in California [Barnes and O'Neil, 1969], groundwater in 434 peridotite catchments in Oman can be divided into two types. MgHCO₃-rich "Type I" waters, with pH \sim 435 8.5 to 10, are common in pools and running water in wadis, and in most shallow wells. These waters 436 437 are thought to be produced by near-surface weathering of the peridotite, dissolving Mg²⁺, together 438 with uptake of CO₂ from the atmosphere to form bicarbonate. 439

End-member, Ca(OH)₂-rich, "Type II" waters have pH > 10, and are generally restricted to alkaline springs with associated travertine deposits, and some wells in peridotite. These waters are thought to form via more extensive, perhaps deeper interaction between ground water and peridotite. Mg and CO₂ are lost, due to precipitation of serpentine and carbonate minerals, while Ca²⁺ is dissolved along the flow path. The source of Ca²⁺ could be the peridotite [e.g., *Barnes and O'Neil*, 1969], gabbro and pyroxenite dikes [*Streit et al.*, 2012], and/or calcium-carbonate minerals formed during earlier alteration [*Noël et al.*, 2018].

Both Type I and Type II waters, and apparent mixtures of the two, are present in the aquifers of Wadi
Laywani. Prior to OmanDP, the presence of Type II waters in monitoring well NSHQ14 was known.
Water sampling and geophysical logging of Hole BA1A, drilled in 2017, established that Type 1
waters were also present, particularly at shallow depths, together with relatively fresh, pH 6-8 water at
the top of the Hole which probably represents less modified, recent rainwater. More substantial data
on water composition in the MBO are provided in Section 3.5 and discussed in Section 4.4.

Based on a variety of different lines of reasoning, catchment-scale-, Hole-to-Hole scale-, single Hole scale- and core-sample scale-studies have found that permeability in peridotite hosted aquifers in the Samail ophiolite is > 10^{-14} m2 near the surface, and ~ 10^{-14} to 10^{-15} below ~ 100 m, with considerable Hole to Hole variability in the depth of this transition within the MBO [*Dewandel et al.*, 2005; *Dewandel et al.*, 2004; *Katayama et al.*, 2020; *Katayama et al.*, 2021; *Lods et al.*, 2020].

2. Methods

2.1 Core description

Cores were curated on the drill site and then described onboard Drilling Vessel (DV) Chikyu. In 465 addition to visual core description, analysis onboard DV Chikyu included whole core measurements of 466 magnetic susceptibility, sound wave speed, density, and natural gamma radiation. In addition, all 467 468 cores were analyzed for X-Ray Computed Tomography, and the cut core face was photographed at 469 high resolution. Dozens of thin sections of core samples from Holes BA1B, BA3A and BA4A were prepared, at the University of Southampton and onboard DV Chikyu. X-Ray Diffraction (XRD) 470 measurements were made on powdered samples from core, and from drill cuttings from rotary 471 472 boreholes BA1A, BA2A and NSHQ14. Full thin section photos, in both plane and cross-polarized light, 473 were made onboard DV Chikyu Petrographic descriptions of each thin section were completed by the 474 shipboard science teams. All of these data are available at Texas A&M University by the International Ocean Discovery Program (IODP): http://publications.iodp.org/other/Oman/OmanDP.html, and 475 specifically in Kelemen et al. [Kelemen et al., 2021d; e; f; g]. 476 477

478 Images of shipboard thin sections of core samples from Hole BA1B were obtained using a scanner 479 onboard DV Chikvu [Kelemen et al., 2021d]. The color of these images was characterized at Lamont Doherty Earth Observatory. Red (R), green (G), and blue (B) values (range 0-255) of whole or part of 480 thin section images were determined using ImageJ [Abràmoff et al., 2004]. Redness, greenness, and 481 blueness (range 0-1) was calculated from RGB values, normalized to 255, by subtracting the value of 482 the color of interest with the average of those of the other two colors. Redness and greenness values 483 484 used in Figure 11 were renormalized to values between 0 and 1 via (observed value - minimum value 485 for BA1B sections)/(maximum - minimum value for BA1B sections. Total RGB (R+G+B) was

486	calculated to quantify brightness. Another measure for lightness or brightness, luminosity (Y), was
487	calculated using the SMPTE-C (Society of Motion Picture and Television Engineers) RGB luminance
488	Values $Y = 0.21R + 0.72G + 0.07B$.
489	
490	2.2 Whole rock geochemistry
491	
492	Major, minor and trace element analyses, including volatile species CO ₂ (all C as CO ₂), H ₂ O and total
493	sulfur were made by the OmanDP Science Team onboard Drilling Vessel Chikyu, and during
494	laboratory work at the Université de Montpellier generously done by Marguerite Godard and
495	colleagues to check and complete the "shipboard" geochemical dataset. XRF major and minor
496	element analyses of a subset of samples were also conducted at the University of St. Andrews, which
497	allowed cross-calibration with shipboard whole rock data. Methods used to obtain these data are
498	described in Kelemen et al. [2020c] and results are reported in Kelemen et al. [Kelemen et al., 2021d:
499	f: g] hosted online at http://publications.jodp.org/other/Oman/OmanDP.html
500	r, gj, notioù oninio at <u>mpi/publicationolioùpiog/otnol/ornali/ornalionalibrintan</u> .
500	FeO contents of shiphoard rock powders from core from Hole BA1A were measured at the
507	Geoscience Laboratories of the Ontario Geological Survey, using methods described online at
502	bttps://www.mpdm.gov.op.op/pitos/dofoult/filos/2021.goo.lobs.broshuro.pdf. It is possible that come
505	redev consistive minorale become evidiand prior to englyzic (for evential brueite may become
504	redux-sensitive minerals became oxidized phor to analysis (for example, bruche may become
505	oxidized in air within a matter of days, Ellison et al. 2021). Fe2O3 contents of our samples were then
506	estimated by subtraction of these FeU contents (recalculated as Fe ₂ U ₃ from total iron measured as
507	Fe2O3 onboard DV Chikyu. Supplementary Table S1 reports the shipboard geochemical information
508	for Hole BA1B [Kelemen et al., 2021d], plus FeO contents.
509	
510	Normative "igneous" mineralogy for gabbroic samples in core from Hole BA4A was calculated from
511	the bulk compositions using a standard CIPW norm, assuming all Fe as FeO since magnetite was not
512	reported to be abundant in these samples. Normative serpentinite mineralogy for dunite and
513	harzburgite samples in core from Hole BA1A, in terms of Ca-Mg-Fe carbonates, Mg-FeII lizardite, Mg-
514	Fe brucite, and either FeIII cronstedtite or Fe(OH) ₃ , was calculated by mass balance, using measured
515	SiO ₂ , CO ₂ , CaO, MgO, FeO, and Fe ₂ O ₃ contents of our samples, "projected" from other elements. Mg
516	and Fe ²⁺ were treated identically, so that lizardite, brucite, magnesite and cronstedtite all had the
517	same Mg/(Mg+Fe ²⁺). All CaO was assigned to calcite. Remaining CO ₂ was assigned to magnesite. All
518	Fe ³⁺ was assigned to either cronstedite or Fe(OH) ₃ . The normative proportions of these minerals were
519	used to calculate a maximum weight percent H ₂ O, if all Mg and Fe in the rocks were in carbonates
520	plus hydrous minerals, for comparison to observed H ₂ O contents in the samples. The resulting
521	serpentinite norms are also included in Supplementary Table S1.
522	
523	2.3 Electron microprobe analyses of minerals
524	
525	Compositions of minerals in polished thin sections were quantitatively analyzed using a 5-
526	spectrometer Cameca SX-100 electron microprobe (EMP) at the American Museum of Natural History
527	(AMNH) Calibration was performed using in-house natural and synthetic standards. A grain of San
528	Carlos oliving was measured multiple times as unknowns during the experimental run $(n=9)$ with all
520	major elements within error of the known composition. Semi-quantitative elemental mans of Ni and S
520	were obtained by electron dispersive spectroscopy (EDS) using the new 5-spectrometer Cameca
530	SYE Tactic at AMNH, operating conditions were 15k/ and 40nA. Images were past processed using
531	Apple Color Syna Litility to increase exposure and sharphase. Atomic units of major elements in
532	Apple Color-Sync Olling to increase exposure and sharpness. Atomic units of major elements in minorely were calculated from weyelength dispersive energies and the Volues for chlorite.
533	minerals were calculated from wavelength dispersive spectroscopy (wDS) data. Values for chlorite
534	and serpentine were calculated assuming 14 and 7 oxygen atoms per formula unit, respectively. For
535	chlorite minerals (including amesite), Fe st atoms per formula unit were calculated assuming no site
536	vacancies. Electron microprobe WDS data used to calculate mineral compositions are provided in
537	Supplementary Table SZ.
538	
539	2.4 Analysis of carbonate veins
540	
541	Carbonate mineral identification by X-Ray diffraction (XRD) was performed at Lamont Doherty Earth
542	Observatory (LDEO) using an Olympus BTX-II XRD analyzer. Diffractograms were analyzed using
543	Match! Software.
544	

545 For Sr isotope analysis of carbonate veins, carbonate powder was dissolved in glacial acetic acid. To 546 remove any remaining acetic acid the solution was dried, dissolved in HNO₃ and redried. The residue 547 was redissolved in 3N HNO₃ prior to column chemistry using the Eichrom® Sr resin. Purified Sr splits were analyzed for isotopic compositions with the standard bracketing method using the US National 548 Institute of Standards and Technology (NIST) SRM 987 on a Thermo Scientific Neptune multi-549 collector ICP-MS at Lamont Doherty Earth Observatory (LDEO). In-run mass fractionations were 550 normalized to ⁸⁶Sr/⁸⁸Sr=0.1194. Unknowns were normalized to SRM 987 ⁸⁷Sr/⁸⁶Sr value of 0.701248. 551 International standards BHVO-2 yielded ⁸⁷Sr/⁸⁶Sr value of 0.703474±20 (2s, n = 2) and BCR-2 yielded 552 0.705010±18 (2s), which agree with published values from Weis et al. [2006]. 553

554

555 Radiocarbon analysis were performed at The National Ocean Sciences Accelerator Mass

556 Spectrometry (NOSAMS) facility at Woods Hole Oceanographic Institution, using methods described 557 online at https://www2.whoi.edu/site/nosams/ . We sent clean but not etched, carbonate fragments to 558 NOSAMS, where they performed a pre-etch in 10% hydrochloric acid at room temperature to remove 559 modern atmospheric CO₂ adsorbed on mineral surfaces.

560

Additional analyses of δ^{13} C, together with δ^{18} O, in carbonate minerals, were performed at LDEO using a Thermo-Fisher Delta V+ mass spectrometer with dual-inlet and Kiel IV carbonate reaction device. Powdered carbonate samples were acidified in the Kiel IV device using ~105% H₃PO₄ at 70C for 10 min before transferring the CO₂ to the Delta V+. The standard deviation of NBS-19 standards analyzed (n=6) was 0.03‰ for δ^{13} C and 0.06‰ for δ^{18} O.

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Isotope ratio data on carbonate veins are reported in Supplementary Table S3.

569 570

2.5 Thermodynamic modeling of water/rock reaction

Simulations of water-rock interactions used the speciation and reaction-path code, EQ3/6 [T Wolery 571 and Jarek, 2003; T.J. Wolery, 1992]. Reaction progress of the water-rock interaction process is 572 quantified by decreasing the water-rock mass ratio (W/R), and simulates a given mass of fluid 573 reacting with an increasing mass of rock as it infiltrates an aquifer. A global average rainwater 574 575 composition compiled by Hao et al. [Hao et al., 2017] from Berner and Berner [Berner and Berner, 576 2012] was used in the models. The composition of average harzburgite used in the simulations was 577 calculated from the data of Hanghoj et al. [Hanghoj et al., 2010], including average Cu (20 ppm) and 578 Ni (2000 ppm). We used 300 ppm total sulfur in the reacting harzburgite, which is higher than the range of 6 to 100 pmm measured by Hanghoj et al., but in the 100-500 ppm range measured by 579 Oeser et al. [Oeser et al., 2012] in Samail ophiolite peridotites. Compositions of reacting rainwater 580 581 and harzburgites are shown in Supplementary Table S4. 582

- The thermodynamic data used in the simulations are from Klein et al. [2013]. They include data for relevant oxides, sulfides, native metals, and alloys from Klein and Bach [2009], Klein et al. [2009], Helgeson et al. [1978], Leong and Shock [2020] and Wolery and Jove-Colon [2004], and aqueous fluid values from Shock and Helgeson [1988], Shock et al. [1977], and Sverjensky et al. [1997] calculated using the SUPCRT code [*Johnson et al.*, 1992]. The database allows formation of serpentinization-relevant minerals in ideal-site solid solutions and has been successfully used in previous works [*de Obeso and Kelemen*, 2020; *Klein et al.*, 2009; *Klein et al.*, 2013].
- 591 As with Bruni et al. [2002], Paukert et al. [2012] and Leong et al. [2021b], thermodynamic simulations 592 were divided into two steps, both at 35°C. The first step involves reaction of rainwater with peridotites open to the atmosphere from water-rock ratios 10,000 to 10 (i.e., reaction of 1 kg of rock in 10 kg 593 water). The second step involves reaction of fluids generated at the end of first step with the same 594 peridotite, closed to atmospheric input. The first step simulates reactions close to the surface while 595 the second step models reactions in deeper aquifers. In contrast to Paukert et al. [2012] and Leong et 596 597 al. [2021b], first step simulations in this work were allowed to run to higher reaction progress (i.e. towards lower W/R ratio, down to ~10) until modeled dissolved sulfate concentrations approximate 598 field constraints before proceeding to the second step. Results of calculations are shown in Figure 29, 599 for the first and second steps, respectively, and in Supplementary Table S4. The first step produces 600 with composition similar to natural, Mg-HCO3-rich "Type I" fluids from shallow peridotite aquifers, while 601 the second step yields fluids with compositions similar to Ca-OH-rich "Type II" fluids found at 602 603 peridotite-hosted alkaline springs and deep boreholes, as originally outlined in the classic paper of 604 Barnes and O'Neil [Barnes and O'Neil, 1969].

Using a comprehensive compilation of published data on fluids from peridotite-hosted springs and
wells in the Samail ophiolite, the extent of disequilibrium (in kilojoules per mole) between these fluids
and chrysotile and brucite was calculated using EQ3/6 with the same thermodynamic data as above,
with oxygen fugacities calculated using the published Eh, pH and temperature data [*Canovas et al.*,
2017; *J A M Leong et al.*, 2021b; *Nothaft et al.*, 2021a; *Nothaft et al.*, 2021b; *Paukert et al.*, 2012; *Paukert Vankeuren et al.*, 2019; *Rempfert et al.*, 2017]. Results are shown in Supplementary Figure 1.
In addition, the extent of disequilibrium for the chrysotile-brucite reaction

$$Mg_{3}Si_{2}O_{5}(OH)_{4(chrysotile)} + H_{2}O = 3Mg(OH)_{2(brucite)} + 2SiO_{2(aq)}$$
(1)

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613

and the cronstedtite-ferrous brucite (or ferrous hydroxide) reaction

617

618 619 $Fe^{2+}{}_{2}Fe^{3+}SiFe^{3+}O_{5}(OH)_{4(cronstedtite)} + H_{2}O + H_{2} = 4Fe(OH)_{2(Fe-brucite)} + SiO_{2}$ (2)

were also calculated for the compiled data on Samail ophiolite fluids, with results shown in 620 621 Supplementary Figure 2. In Supplementary Figures 1 and 2, values with positive ΔG_r indicate that the 622 reactant side of the reaction is favored, *i.e.*, brucite is metastable with respect to serpentine in all of the peridotite-hosted fluids analyzed so far. Continuing in this theme, we calculated fO₂ for these 623 624 fluids, using measured Eh, pH and temperature, as outlined in Section 2.6. While some of the most 625 reduced fluids closely approach (on a log scale!) the low fO₂ limit where water breaks down to form 626 H_2 , $2H_2O = 2H_2 + O_2$, no fluids sampled so far are calculated to be saturated in H_2 gas (Supplementary Figure 3), consistent with the observation that to date, no gas tight samples from 627 deep boreholes have been H₂ saturated, though a few have dissolved H₂ concentrations within a 628 factor of 10 of the saturation value at a the depth of sampling (Hoelher, pers. comm. 2021). 629 630

631 fO₂ and fS₂ values set by assemblages composed of oxides, sulfides, alloys and native metals were calculated using the same thermodynamic data as above. An fO2 vs fS2 diagram at 35 °C was created 632 633 using Geochemist's Workbench [Bethke, 1998]. While these minerals provide constraints on the 634 redox conditions at which they precipitated, fO₂ is likely set by reactions involving major elements 635 (i.e., Fe). Hence, fO_2 set by reactions involving Fe endmembers of brucite (Fe²⁺(OH)₂) and serpentine were also calculated. Fe endmembers of serpentine used in calculations are Fe²⁺-serpentine 636 (greenalite, Fe²⁺₃Si₂O₅(OH)₄), Fe³⁺-serpentine (hisingirite, Fe³⁺₂Si₂O₅(OH)₄), and mixed-valence 637 serpentine (cronstedtite, $Fe^{2+}_{2}Fe^{3+}Si Fe^{3+}O_{5}(OH)_{4}$. In addition, we calculated fO₂ set by reactions 638 involving Mg-endmember cronstedtite (Mg₂Fe³⁺SiFe³⁺O₅(OH)₄) together with Mg-brucite (Mg(OH)₂), 639 Mg-serpentine (chrysotile, $Mg_3Si_2O_5(OH)_4$), greenalite, and Fe-brucite. We found that calculations 640 using Mg-cronstedtite can better account for the Fe³⁺/ Σ Fe determined from the cores (up to 0.9) as it 641 allows total oxidation of all reacting ferrous iron. In contrast, using Fe-cronstedtite only allows up to 642 50% oxidation of starting ferrous iron. Reaction stoichiometries involving these minerals in 643 644 calculations of fO_2 are explicitly provide throughout the discussion.

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646 Early theoretical work on redox conditions attained during serpentinization focused on reactions that 647 involved minor phases (sulfides, oxides, alloys, native metals) and reactions involving Fe²⁺-648 serpentine/talc [Frost, 1985; Frost and Beard, 2007]. Mineral analysis showed that serpentine can 649 incorporate both ferrous and ferric iron into its crystal structure [Andreani et al., 2013; L. E. Mayhew 650 and Ellison, 2020; D. S. O'Hanley and Dyar, 1993]. Thus, more recent studies often incorporate mixed-valence serpentine (i.e., Fe- and/or Mg-cronstedtite) into thermodynamic models [KA Evans et 651 al., 2013; Klein et al., 2013; Lazar, 2020; J A M Leong and Shock, 2020; B. M. Tutolo et al., 2019; B. 652 M. Tutolo et al., 2020; Zolotov, 2014] (Klein et al., 2013; Zolotov, 2014; Evans et al., 2013; Tutolo et 653 al., 2019; 2020; Lazar, 2020; Leong and Shock, 2020). Oxidation of ferrous iron hosted in MgFe²⁺-654 brucite and MgFe²⁺-serpentine into ferric iron in cronstedtite (\pm hisingirite) is dependent on the SiO₂ 655 activity constrained by these mineral assemblages. In this work, calculations incorporating variable 656 SiO₂ activities were used, ranging from a(SiO₂) dictated by Mg-serpentine (chrysotile) and Mg-brucite 657 to higher a(SiO₂) dictated by Mg-serpentine and talc. These, encompass the range of a(SiO₂) in pH 658 >9 fluids from the Samail ophiolite [J A M Leong et al., 2021b]. 659

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2.6 Downhole logging of borehole water Eh, pH, conductivity, temperature and pressure

663 Borehole water properties were measured via wireline logging using slimline QL40-Ocean, QL40-664 MUSET and Robertson water quality probes as described in Kelemen et al. [*Kelemen et al.*, 2020c]. The oxidation-reduction potential measured by the Ag/AgCl electrode (E_{measured}, in volts) was
 converted to E_h (relative to the standard hydrogen electrode, in volts) using a temperature-dependent
 calibration based on data provided by the manufacturer:

$$E_{\rm h} = E_{\rm measured} + 0.22323 - 0.001046(T - 298.15)$$
(3)

Where T is the measured temperature in Kelvin. For oxygen reduction the standard reduction
 potential E⁰ (in volts) can be calculated:

$$E^{0} = 1.2291 - 0.0008456(T - 298.15)$$
⁽⁴⁾

676 [*Bratsch*, 1989]. Then oxygen fugacity was calculated by solving the Nernst Equation as a function of E_h, pH and
 677 temperature:
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$$\log(fO_2) = \frac{4F}{RTln(10)}(E_h - E^0) + 4pH$$
(5)

681 in which R is the universal gas constant, and F is Faraday's constant. It should be noted that a single systemwide Eh value cannot be defined or measured when this method is applied to fluids that contain significant 682 concentrations of multiple, redox sensitive solutes (e.g., O₂, H₂, Fe²⁺, Fe³⁺, H₂S, SO₄²⁻, NO³⁻, NH₃ subject to 683 electron transfer via NH₃ to NO³⁻, H₂S to SO₄²⁻, Fe²⁺ to Fe³⁺, H₂ to H₂O or H⁺, and so on), that are not in mutual 684 685 equilibrium. Different species may record different redox potentials [e.g., Shock et al., 2010], and the reference 686 electrode may not respond to the various dissolved redox-sensitive species equally [Anderson, 2017; Lindberg 687 and Runnells, 1984]. However, among these, H₂ is the most abundant species in serpentinization-generated fluids at depth. For example, Supplementary Figure S4 illustrates that the concentration of dissolved H2 in 688 689 borehole water samples from the Samail ophiolite is greater than or equal to the combined concentration of all 690 other redox sensitive solutes. As a result, the measured Eh and derived fO2 are likely to correspond well (on a 691 log scale!) to dissolved H₂ concentrations. 692

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 $\log(fO_{2(\text{limit})}) = -E^0 \frac{4F}{RT\ln(10)} - 2\log(P)$ (6)

700 where P is the measured pressure in bars.

702 We estimated the uncertainty on log(fO2_in_bars) and log(fO2_limit_in_bars) based on manufacturer reported uncertainties in the measured E_h (σ_{Eh}) of 1 mV, pH (σ_{PH}) of 0.01, temperature (σ_T) of 0.005°C, and pressure (σ_P) 703 704 of 0.5 bars. Practical uncertainties of field-based measurements were determined by multiplying the 705 manufacturer specifications for uncertainty of the instruments by a factor of 10. The uncertainty on log(fO₂), 706 $\log(fO_2(\text{limit}))$, and the difference $\Delta \log(fO_2) = \log(fO_2) - \log(fO_2(\text{limit}))$ were calculated from the uncertainties on 707 the individual measurements using standard error propagation (Supplementary text, Section 3). While the uncertainties vary slightly as functions of Eh, pH, T, and P, they are consistently less than 1 log unit, and 708 709 therefore we have used ± 1 log unit as the estimated upper bound uncertainty for these measurements. 710

3. Results

3.1 Major elements

Figure 6 illustrates downhole variation of major elements in core from Hole BA1B [*Kelemen et al.*,
2021d]. Similar plots for Holes BA3A and BA4A can be found in Kelemen et al. [2021f; g]. While the
other two Holes do not show systematic variation in bulk composition with depth, Hole BA1B extends
400 meters below the surface, 100 meters deeper than the other two Holes, and this reveals trends
that might not be apparent in the others.

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723 Figure 6: Major element variation in core from Hole BA1B [Kelemen et al., 2021d]. Light green circles: dunites, dark green squares, harzburgite. Small red squares, five point running average of harzburgite compositions.

726 As expected, there is a sharp break between harzburgite and dunite compositions in all three holes, 727 with dunites having higher total iron (expressed as Fe₂O₃T) and MgO concentrations, and lower SiO₂ 728 and CaO contents. Fe₂O₃T contents in dunites are ~ 30% higher than in harzburgites (~ 12 vs 8 wt%), whereas MgO is only ~ 7% richer in dunites compared to harzburgites (~ 47 vs 44 wt%). As a result, 729 molar Mg# (molar MgO/(MgO + FeOT), where all Fe is expressed as FeO) is systematically lower in 730 dunites compared to harzburgites, as illustrated and discussed in Section 4.1. 731

Calcic pyroxenes (cpx) and orthopyroxenes (opx) in Samail ophiolite mantle peridotites typically 733 734 contain ~ 24 and 1 to 2 wt% CaO respectively [M Godard et al., 2000; Hanghøj et al., 2010; Monnier et al., 2006]. As a result, normative mineral compositions for these samples, in terms of olivine, cpx, 735 opx and spinel, contain less than 5% cpx, and would commonly contain no cpx when opx contains 736 several wt% CaO at high temperature. However, these samples have have been substantially 737 modified by later alteration, as discussed further in Section 4.3, and their high temperature CaO 738 contents may have been obscured by this process, 739

3.2 Whole rock alteration

Peridotite core samples from Hole BA1B are pervasively altered, with typical mesh-textured 743 serpentinites near the surface, containing some relict olivine and pyroxene grains at depth. This 744 qualitative observation is quantified in Figures 7 to 16, illustrating systematic decreases in CO₂, H₂O 745 746 and S contents with increasing depth. These trends are apparent for harzburgites and dunites together, and for harzburgites alone. This is important, because Samail ophiolite dunites are more 747 serpentinized than other peridotites (e.g., \[Kelemen et al., 2021d; e; f; g; h; i] so that lithological 748 749 variation alone – with dunites at the top of the hole and harzburgites at greater depth – could give rise 750 to a downhole trend. However, the data from Hole BA1B illustrate a trend that is independent of lithology. These systematic trends are also evident in data on physical properties, from continuous, 751 automated logs of the entire core and shipboard analyses of discrete samples (Figure 7). Downhole 752 753 variation in the concentration of volatile components is less apparent in core from Hole BA3A and 754 BA4A, as can be seen in plots similar to Figure 8 in Kelemen et al. [2021f; g]. 755

756 Figure 9 illustrates normative proportions (in weight units) of Mg-Fe²⁺-serpentine, Mg-Fe²⁺-brucite and 757 Fe(OH)₃ calculated from whole rock compositions, projected from calcite and magnesite. Harzburgites 758 contain more SiO₂ than dunites, and thus generally have a higher serpentine/brucite ratio. 759

760 The normative mineral proportions can then be used to calculate how much H₂O a fully hydrated peridotite of a given bulk composition could contain. These H₂O contents can then be compared to 761 measured bulk rock H₂O concentrations, to quantify the percent hydration of each sample, illustrated 762 in the righthand panel of Figure 8. As expected, dunites are almost fully hydrated, whereas 763 harzburgites record ~ 65 to 100% hydration. Less predictably, the extent of harzburgite hydration 764

765 decreases downhole, as does the calculated proportion of brucite in harzburgite (not shown).

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depth (m)



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depth

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depth



Figure 8: Volatile contents of core from Hole BA1B [Kelemen et al., 2021d]. Righthand panel illustrates the "percent of maximum hydration", based on observed H_2O contents divided by water content of a completely hydrated rock, determined from normative proportions of calcite, magnesite, lizardite, brucite and ferrihydrite

calculated from the major element and CO_2 contents of each sample. Only three harzburgites contain "negative

brucite". If fully hydrated, these three samples would contain some talc, rather than brucite). We also calculated
 mineral norms with all Fe3+ in Mg-Fe2+-cronstedtite rather than Fe(OH)3. This yields higher normative

proportions of brucite in all samples. Symbols as in Figure 6.





Figure 9: Normative proportions of lizardite, brucite and ferrihydrite, projected from calcite and magnesite, in core from Hole BA1B, calculated from the major elements and CO_2 contents of each sample. Symbols as in Figure 6.

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Full thin section images of core samples from Hole BA1B reveal a pattern of color variation, with red, 783 "rusty" sections predominant at the top, a zone of "black serpentinites" at ~ 50 to 150 meters depth, 784 and green, partially serpentinized peridotites in cores from the deeper part of the hole. Figure 10 785 provides end-member examples of these three color zones. The red and green color variations are 786 787 present, but less marked, in core from Holes BA3A and BA4A; the black zone was only prominent in 788 core from Holes BA1B and BA4A. We used image analysis of thin sections to quantify these variations for all of the shipboard thin sections from Hole BA1B. High "redness and low "greenness" 789 790 characterize the rusty colored sections, low luminance characterizes the black serpentinite sections, 791 and high greenness-redness defines the green sections.

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Figure 10: Representative plane polarized photomicrographs of thin sections of core from Hole BA1B.
Left BA1B_4_2_43_48, 10 m depth, center BA1B_44_2_73_78, 109 m depth, right
BA1B_114_4_51_56, 321 m depth.



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Figure 11: Color data from plane polarized optical measurements of thin sections of core from Hole BA1B. See Section 2.1 for analytical methods. Symbols as in Figure 6.

804 Intuitively, it is obvious that the red, rusty cores contain a higher proportion of ferric to ferrous iron, and indeed this is borne out by our quantitative data (compare Figures 11 and 12). What is less 805 evident is that the black serpentinites - which are not notable for high proportions of opaque, iron 806 807 oxide minerals, nor for exceptional ferric to ferrous iron ratios - have relatively high sulfur concentrations, as documented in Figures 12 and 13. Similar sulfide enrichments are also present in 808 black serpentinites in core from Hole BA4A [Kelemen et al., 2021d], which contain up to 0.4 wt% S 809 (Supplementary Figure S5), though the color zoning in BA4A core is more patchy rather than 810 restricted to a limited depth interval. In contrast, sulfur was below detection limit in all analyzed 811 812 samples from Hole BA3A [Kelemen et al., 2021f].

814 Figure 14 provides X-Ray maps of both S and Ni contents of one black serpentinite sample; sulfur 815 abundances are generally low, but it is clear that sulfur (and Ni) are present in one or more microscopic to sub-microscopic phases, within and rimming serpentine mesh cores. While we are not 816 817 sure of the nature of these phases, we hypothesize that they include tochilinite, valleriite and/or haapalite, mixed sulfide-hydroxide ± carbonate minerals and amorphous materials reported in core 818 from the MBO [Kelemen et al., 2021g; A Templeton et al., 2021; B. M. Tutolo and Evans, 2018] and in 819 weathered serpentines from other localities [Alt and Shanks III, 2003; J. S. Beard, 2000; J. S. Beard 820 and Hopkinson, 2000; Hopkinson et al., 2000; Schwarzenbach et al., 2012]. In some cases, these 821 822 phases may be intergrown with serpentine at the nano-scale (Leong, pers. comm. 2021). 823

The matrix alteration of peridotites in core from the MBO formed oxide, sulfide and metal phases that were identified in thin section via reflected light microscopy onboard DV Chikyu [*Kelemen et al.*, 2021d; f; g], and later verified by electron microprobe analyses [*Eslami et al.*, 2018]. Figure 15 illustrates examples of intergrown heazlewoodite, chalcopyrite, native copper, awaruite, pentlandite and magnetite. These can be used to constrain oxygen fugacity during pervasive matrix alteration, as discussed below and in Sections 4.4 to 4.6.



Figure 12: Sulfur concentration [Kelemen et al., 2021d], and ferric iron/total iron ratio, measured FeO concentration and molar $Mg/(Mg+Fe^{2+})$ ratio in core from Hole BA1B (Supplementary Table S1). Sulfur 835 concentrations below the detection limit of shipboard analyses were assigned a value of 0.01 wt% (100 ppm). 836 Orange bar in lefthand panel illustrates previously measured range of sulfur concentration in mantle harzburgites 837 and dunites in the Samail ophiolite, from 5 to 500 ppm [Hanghøj et al., 2010; Oeser et al., 2012]. Symbols as in 838 Figure 6. 839



840 841

842 Figure 13: Relationship of sulfur content with optical properties of thin sections (Figure 11) and ferric iron/total

iron ratios. As discussed in the text, these relationships indicate that sulfur concentrations are highest in the "black serpentinite zone" extending from ~ 30 to 150 m epth, characterized by low Fe³⁺/FeT, and relatively low in 845 the oxidized, red zone at depths less than 30 m. Symbols as in Figure 6.



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Figure 14: Electron microprobe, X-ray intensity maps for sulfur (left) and nickel (right) in core from Hole BA4A, sample BA4A_82-2 43-45cm, 200 m depth. Field of view, 300 microns tall.



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Figure 15: Observed intergrowths of sulfides, oxides and metals in core. Left: BA1B_118-2_0-7, 330 m depth, center BA1B_132-3_54-59, 371 m depth, and BA3A_79-2-36-41, 199 m depth. Cross polarized reflected light images excerpted from Eslami et al. [*Eslami et al.*, 2018] and Figure F32 in Kelemen et al. [*Kelemen et al.*, 2021f]. Abbreviations used in this figure: HzI: heazlewoodite; Ccp: chalcopyrite; Awr: Awaruite; Mgt: magnetite; PtI: Pentlandite.

Figure 16 illustrates the stability of these minerals at 35°C as a function of oxygen and sulfur fugacity.
Aside from the absence of bornite in our samples, and assuming that intergrown minerals formed in
equilibrium with each other, assemblages juxtaposing (a) chalcopyrite, heazlewoodite and native
copper, and (b) chalcopyrite, pentlandite, magnetite and native copper are indicative of fO₂ close to
the low fO₂ limit where H₂O is reduced to form H₂.



864 Figure 16: Phase diagram in terms of log O₂ fugacity versus log S₂ fugacity, for Fe. Ni and Cu sulfides, oxides 865 and metals at 35°C and 500 bars H₂O, with isopleths for the limit where H₂O is reduced to form H₂ at 1 bar, 50 bars (green) and 500 bars. The positions of other phase fields are not strongly pressure dependent in the range 866 867 of $P(H_2O)$ from 1 to 500 bars. Green fields contain assemblages with native copper and magnetite. \pm 868 heazlewoodite (light green) and awaruite (darker green). Red field contains assemblages with magnetite, native copper and pentlandite. Blue field contains magnetite, chalcopyrite and heazlewoodite. Magnetite, copper and 869 awaruite (Figure 15 center) can coexist along the isothermal, isobaric univariant line between the two green 870 871 fields. Copper, heazlewoodite and chalcopyrite (Figure 15, left) are stable together along the univariant line between the blue and light green fields, at fO₂ from 10⁸⁰ to 10⁵² bars. Only a small corner of field 7, for 872 873 pentlandite-bearing assemblages, is stable at fO₂ above the H₂O-H₂ limit at less than 50 bars total pressure. 874 Pentlandite, magnetite, copper and chalcopyrite (Figure 15, right) can stably coexist along the univariant line between red and blue, restricting fO2 to less than ~ 10⁸² bars. Abbreviations for minerals: Py - pyrite, Ccp -875 chalcopvrite, Pdy - polydymite, MIr - millerite, Hzl - heazlewoodite, Po - pyrrhotite, Pn - pentlandite, Mag -876 877 magnetite, Gth - goethite, Awr - awaruite, Cu - copper, Cct - chalcocite, Cpr - cuprite, Bun - bunsenite.

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3.3 Vein types and proportions

The Proceedings of the Oman Drilling Project include extensive information about the different types
of veins cutting the mesh-textured serpentinites in the MBO, and their cross-cutting relationships.
[*Kelemen et al.*, 2021d; f; g]. It is beyond the scope of this paper to review all that material. However,
we can make some important overall points.

First, systematically counting and measuring veins in mesh-textured serpentinite is difficult, because 886 the mesh itself is defined by a grid of ~ 5 to 50 micron wide veins, ~ 50 to 200 microns apart, with 887 "mesh cores" between them. The shipboard science teams tried not to include the frequency or 888 889 volume of mesh veins in their logging, but this may have led to systematic errors that differed from observer to observer, and from day to day, particularly as the team became more familiar with subtle 890 features of the core. Figure 17 provides an example of a black magnetite-serpentine vein cutting 891 892 across the mesh texture. Depending on the level of scrutiny, the nature of the cut core face, and other factors, veins like this one could have been logged, or missed. 893 894



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Figure 17: Composite, plane polarized, transmitted light image of a long, black, magnetite-serpentine vein extending horizontally across the image, cutting earlier mesh texture in serpentinized peridotite. Sample BA1B 26-3_42-45, 57 m depth. Image from Figure F27 in Kelemen et al. [Kelemen et al., 2021d]. Width of image, approximately 4.1 millimeters. During visual core description, mesh veins were not logged, but it was often difficult to distinguish between mesh veins and early serpentine-magnetite veins like the one shown here.

Second, as noted in Section 1.4, the veins could record a variety of different events and conditions, 903 904 potentially ranging from early hydrothermal alteration near an oceanic spreading center, extending 905 into the shallow mantle, through Cretaceous subaerial weathering and by a Late Cretaceous marine 906 transgression, to present day weathering. While cross-cutting relationships provide an indication of relative age, they do not provide absolute age information. 907 908

Third, the two youngest vein types, based on consistent cross-cutting relationships, were "waxy 909 veins" and carbonate veins. The first group has an aphanitic, glossy appearance on the cut core face. 910 In thin section, these veins have isotropic to microcrystalline serpentine cores, often flanked by fibrous 911 microcrystalline rims with elongate crystals perpendicular to vein contacts. At the thin section scale, 912 913 the vein contacts are sharp, but curved and irregular rather than planar. Intially this vein type was 914 named "waxy green veins", but toward the bottom of Hole BA1B, and deep in the other two cored 915 holes, the same textures were seen in white veins, so the color adjective was drooped.

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Figure 18: Transmitted light photomicrographs of waxy serpentine veins. Left, plane polarized light image, white carbonate vein cuts (?) brownish waxy serpentine vein, which in turn cuts serpentite mesh texture and a set of grey, intermediate-aged, coarse serpentine veins, BA1B_23-4_37-41. Center (plane-polarized) and right (crosspolarized light) images of vein containing intergrown carbonate and waxy serpentine, cutting mesh textured 922 923 serpentinite. Serpentine is brown in plane light, with bright-grey interference colors in cross-polarized light; 924 coarse single crystal of carbonate is tan in both images, and contains twin planes that diagonally intersect grain boundaries. BA1B_17-1_22-22.5. Righthand pair of photos kindly provided by Wolf-Achim Kahl. 925

927 The carbonate veins were typically logged as calcite veins, particularly early in the description of core 928 from Hole BA1B, and in almost every instance when the vein material effervesced in dilute HCI. However, XRD analyses performed at Lamont Doherty Earth Observatory demonstrate that most of 929 these veins contain dolomite, aragonite, magnesite, and huntite (a hydrous Mg-carbonate), instead of, 930 or in addition to, calcite (Supplementary Table S3). ¹⁴C, ⁸⁷Sr/⁸⁶Sr and stable carbon and oxygen 931 isotope data on a subset of the carbonate veins are presented in Section 3.4. 932

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Carbonate veins and waxy veins are commonly intergrown, as shown in Figure 18, indicating 934 approximately coeval formation, at least in some instances. Waxy veins, particularly in the deeper 935 parts of BA1B and throughout BA4A, commonly cut contacts between gabbroic veins and surrounding 936 937 serpentinites.

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Figure 19: Typical textures of waxy serpentine veins in photographs of cut core face [Kelemen et al., 2021g], with field of view about 8 cm tall. Left: BA4A-88Z-3_8-18, 238 meters depth, "turtle-textured" grid of intersecting veins, right: BA4A-88Z-4_4-24, 240 m depth, veins cutting altered gabbro dikes, extending a few cm into serpentine 943 944 surrounding the dike margins.

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946 Serpentine in waxy veins from one sample of BA1B core contains relatively low SiO₂ contents, and 947 several weight percent Al₂O₃, indicative of substitution towards the amesite mineral end member

948 (Figure 20, data in Supplementary Table S2). Similarly, elsewhere in the Samail ophiolite and 949 probably in BA1B core, serpentines have relatively low SiO₂ and high Fe, interpreted to be due to 950 appreciable amounts of the cronstedtite substitution ((Mg, Fe^{2+})₂Fe³⁺SiFe³⁺O₅(OH)₄). On the other 951 hand, analyses of waxy serpentine veins in a sample of core from Hole BA3A have very low AI and 952 Fe³⁺ contents, and approximately 2 Si per formula unit. It's likely that continued analyses of the cores 953 will reveal gradients in serpentine contents with depth in BA1B, and generally lower Fe³⁺ in BA3A 954 serpentines.



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958 Figure 20: Silicon and aluminum contents of waxy serpentine veins in core from BA1B 17-1 22-25.5, 33 meters depth (filled green circles), cutting an altered gabbroic dike and extending into mesh-textured serpentinite, and 959 BA3A 43-3 24-27, 100 m depth (filled grey circles) cutting mesh-textured serpentinite without gabbroic dikes. 960 961 These data are, compared to analyses of low temperature serpentine veins formed by young weathering (< 962 50,000 years, open orange circles, Streit et al. [2012] and by weathering from just below an unconformity overlain by Late Cretaceous limestones (open brown circles, de Obeso and Kelemen [2018; 2020]. Filled diamonds are 963 964 compositions of serpentine produced in experiments saturated in Al₂O₃; blue: Wang et al. [Wang et al., 2020]; 965 red: Pens [Pens et al., 2016]. All concentrations determined by electron microprobe as described in Section 2.3. 966 Calculated Si and Al apfu values are based on 7 oxygen atoms. Dark green dashed line indicates mixtures of chrysotile/greenalite and amesite. Filled dark green circles are labeled with mole % amesite in these mixtures. 967 Abbreviations for minerals: Ctl – chrysotile ($Mg_3Si_2O_5(OH)_4$), Gre – greenalite ($Fe^{2+}_3Si_2O_5(OH)_4$), Kln – kaolinite ($Al_2Si_2O_5(OH)_4$), Ctd – Mg_Fe^{2+} -cronstedtite (($Mg_Fe^{2+})_2Fe^{3+}Si_Fe^{3+}O_5(OH)_4$), Brc – Mg_Fe^{2+} -brucite (($Mg_Fe^{2+})_2Fe^{3+}Si_Fe^{3+}O_5(OH)_4$), Ctd – $Mg_Fe^{2+}Si_Fe^{3+}Si_Fe^{3+}O_5(OH)_4$), Ctd – $Mg_Fe^{2+}Si_Fe^{3+}Si_Fe^{3+}O_5(OH)_4$), Ctd – $Mg_Fe^{2+}Si_Fe^{3+}Si_Fe^$ 968 969 Fe^{2+})(OH)₂), Ame – Mg- Fe^{2+} -amesite ((Mg- Fe^{2+})₂AlSiAlO₅()OH)₄). 970 971

Together with relatively Al-rich serpentine, some waxy veins contain andradite-hydrogrossular garnet
 solid solutions, and microcrystalline chlorite (Figure 21, data in Supplementary Table S2). Together
 with the common spatial association of waxy veins with gabbroic dikes, these observations suggest a
 role for Al in stabilizing serpentine minerals that grow at a geologically appreciable rate in the low
 temperature weathering environment (rates discussed in Section 4.7).

Fourth, the abundance of carbonate veins declines steeply from a few volume percent in the upper tens of meters (poorly sampled during drilling) to near zero in cores from more than 100 m below the surface (Figure 22). The frequency of waxy veins also shows a general decrease with depth in core from Hole BA1B, though no trend is evident in the other two cores. Older sets of black, white and composite serpentine veins do not show systematic variation in frequency with depth. Overall, all cored MBO Holes show decreasing area proportion of veins with increasing depth (Figure 23).



987 Figure 21: Silicon and aluminum contents of microcrystalline chlorite in waxy serpentine veins cutting an altered 988 gabbroic dike and surrounding, mesh-textured serpentinite (filled green circles, BA1B 17-1 22-25.5, 33 meters depth) compared to chlorite in altered gabbros near OmanDP Site GT1 (orange circles, Zihlmann et al. [2018] 989 990 and in altered oceanic crust (brown circles, Alt and Bach [2001]. Calculated Si and Al apfu values are based on 991 14 oxygen atoms. Endmember minerals are indicated by the blue squares and dashed blue lines. Analyses 992 indicate that the natural chlorites are mixtures including clinochlore (Clc, Mg5AISi3AIO10(OH)8), daphnite (Dph, 993 Fe5AlSi3AlO10(OH)8, aka chamosite), sudoite (Sud, (Mg-Fe²)2Al3Si3AlO10(OH)8, Mg-Fe²⁺-chrysotile (Ctl, (Mg- $Fe^{2+})_6Si_4O_{10}(OH)_8)$, Mg- Fe^{2+} -amesite (Ame, (Mg- $Fe^{2+})_4Al_2Si_2Al_2O_{10}(OH)_8)$, Mg- Fe^{2+} -talc (Tlc, (Mg- $Fe^{2+})_3Si_4O_{10}(OH)_2$), pyrophyllite (Pyp, $Al_2Si_4O_{10}(OH)_2$), beidellite (Bei, $K_{0.33}Al_2Si_{3.67}Al_{0.33}O_{10}(OH)_2$), 994 995 montmorillonite (Mnt, Cao.17(Mg, Fe²⁺)0.33Al1.67Si4O10(OH)2), and/or saponite (Sap, Cao.17(Mg, Fe²⁺)3Si3.67 996 997 Al_{0.33}O₁₀(OH)₂. Clinochlore, daphnite, and sudoite endmembers belong to the chlorite group of minerals. 998 Chrysotile and amesite endmembers belong to the serpentine group while beidellite, montmorillonite, and 999 saponite endmembers are clay minerals. The chrysotile and amesite endmembers used in this figure are two 1000 times the formula units used in Figure 20 to be consistent with chlorite stoichiometry (2x serpentine). 1001



Figure 22: 25 meter running average vein frequency from shipboard visual core description, Left: Figure F30 from 1004 Kelemen et al. [Kelemen et al., 2021d]. Center: Figure F28 from Kelemen et al. [Kelemen et al., 2021f]. Right: 1006 Original plot from data in Kelemen et al. [Kelemen et al., 2021g].





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1010 Figure 23: Core section and running average data on vein area, in units of percent volume fraction of the core, calculated from vein widths and frequency data from shipboard visual core description logs. Left: Figure F28 from 1012 Kelemen et al. [Kelemen et al., 2021d]. Center: Figure F27 from Kelemen et al. [Kelemen et al., 2021f]. Right: Original plot from data in Kelemen et al. [Kelemen et al., 2021g]. 1013

Fifth, though vein volumes were not well constrained during core description onboard DV Chikyu, a 1015 1016 combination of data on vein frequency and width allowed the shipboard science team to approximately quantify the overall volume fraction of veins in the core as a function of depth. 1017 1018

3.4 Isotopic characteristics of carbonate veins

Supplementary Table S3 reports new data on ¹⁴C, ⁸⁷Sr/⁸⁶Sr, d¹³C and d¹⁸O, collected for this paper. 1021

1022 ¹⁴C contents are reported as fraction modern carbon, and as the ¹⁴C age of samples, assuming they 1023 1024 formed at a single time from a source equilibrated with atmospheric CO₂ at that time. About 2/3 of 1025 analyzed samples contained measurable ¹⁴C (7 of 15 from 3 to 57 m in BA1B, 6 of 6 from 5 to 9 m in 1026 BA3A, 10 of 14 from 1 to 32 m in BA4A). The chances of sample contamination are low - samples 1027 were acid washed to remove young carbon introduced during drilling and sample preparation, and in 1028 any case it is difficult to contaminate carbonate samples with carbonate. Fraction modern ¹⁴C abundances range from zero to 0.0782 ± 0.00001, corresponding to nominal ages ranging from 1029 greater than ~ 50,000 years to 20,300 \pm 100 years. The sample with the lowest measurable ¹⁴C 1030 abundance contains 0.16 ± 0.05 % modern carbon, corresponding to a nominal age of 52,600 ± 2300 1031 years. Thus, about 2/3 of the carbonate veins appear to have formed, or incorporated a young carbon 1032 component, in the last 50,000 years. ¹⁴C abundance does not have any discernable variation with 1033 1034 depth.

1035 d¹³C and d¹⁸O ranges (-5.7 to -16.0 % relative to VPDB, 23.5 to 34.3 % relative to SMOW, 1036 respectively) are similar to those reported for peridotite-hosted carbonate veins sampled from 1037 1038 outcrops and road cuts in Samail ophiolite peridotites, with values that are generally higher than in young travertines deposited at peridotite-hosted alkaline springs. (Kelemen and Matter 2008; 1039 Kelemen et al. 2011; Mervine et al. 2014; Falk et al. 2016; de Obeso and Kelemen 2018). If we apply 1040 published oxygen isotope exchange thermometers for dolomite [O'Neil et al., 1969; Vasconcelos et 1041 al., 2005] together with the observation that present-day Oman well and spring water has d¹⁸O within 1042 two per mil of seawater ($d^{18}O$ SMOW = 0), we obtain temperatures of ~ 10 to 45°C. Using $d^{18}O$ 1043 exchange thermometers for calcite [Chacko and Deines, 2008; O'Neil et al., 1969], applied to d¹⁸O 1044 data for aragonite, yields temperatures of ~ 22 to 50°C. These low temperatures, together with a 1045

mean annual surface temperature of 30°C in northern Oman, and an approximate geothermal
 gradient of 20 to 25°C estimated from temperature profiles measured in MBO boreholes, are
 consistent with the ¹⁴C ages, and both data sets are indicative of vein formation via water-rock
 reaction near the present-day erosional surface.

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Present day ⁸⁷Sr/⁸⁶Sr ratios in eleven carbonate vein samples range from 0.708216 ± 0.000016 to 1051 0.708596 ± 0.000015, averaging 0.708492 ± 0.000066 (2 std error). These values are similar to 1052 ⁸⁷Sr/⁸⁶Sr previously reported for peridotite-hosted spring and well water, and for young, low 1053 temperature carbonate veins, in the Samail ophiolite mantle section [Kelemen et al., 2011; 1054 Weyhenmeyer, 2000]. They are higher than ⁸⁷Sr/⁸⁶Sr in seawater from 20 Ma to 96 Ma [*McArthur et* 1055 1056 al., 2020], where 96 Ma is the age of Samail ophiolite crustal formation and hydrothermal alteration near an oceanic spreading center [Rioux et al., 2012; Rioux et al., 2013; Tilton et al., 1981; Warren et 1057 1058 al., 2005]. However, the Sr isotope ratios in our carbonate vein samples are lower than present-day 1059 seawater and rainwater, most likely due to mixing between a young seawater component and small amounts of mantle-derived Sr with ⁸⁷Sr/⁸⁶Sr ~ 0.703. 1060

3.5 Borehole water properties

Borehole water properties were measured as described in Kelemen et al. [*Kelemen et al.*, 2020c]. We used the measured temperature, pressure, Eh and pH to calculate oxygen fugacity, fO₂, as described in Section 2.6. Downhole variation of water fO₂ and pH is illustrated in Figure 24. Where repeated measurements were made in the same borehole, these are illustrated in separate panels.

1069 In general, pH in borehole waters increases with depth, while fO₂ decreases with depth. Lubrication 1070 for drilling utilized fresh drinking water, thought to be close to equilibrium with air at 1 bar. Thus, 1071 drilling introduced oxidized water into the more reduced, peridotite-hosted aquifer(s). Partly for this 1072 reason, borehole waters have generally become more alkaline and more reduced over time since drilling. Unfortunately, it is not clear whether this results from (1) advective or diffusive mixing of 1073 1074 freshwater introduced during drilling with reduced, alkaline pore water in the surrounding rocks, (2) flow of freshwater away from the Holes, to be replaced by reduced, alkaline pore water from the 1075 1076 surrounding rocks, or (3) reaction between the freshwater introduced by drilling and the surrounding 1077 rocks. 1078

Holes BA1A and BA1D are about 15 meters from each other. They are hydraulically connected at depth, via a fracture network with a permeability ~ 10^{-15} m² [*Lods et al.*, 2020]. Hole BA1B is ~ 105 meters from BA1D and 120 meters from BA1A. Water with intermediate pH near the top of BA1A flows rapidly downward from 25 to 60 meters depth, below which flow rates are too low to measure. Below 150 and 50 meters in BA1A and BA1D, respectively, one year after drilling water the lower half of both Holes had become more alkaline and reduced, with oxygen fugacity approaching the H₂O-H₂ limit.

1086 Unfortunately, water properties in BA1B have only been fully logged once, a month after drilling, 1087 1088 though downhole pH was measured approximately two years later. A second pH log revealed lower 1089 pH in the upper 200 m of the Hole, and higher pH in the lower half of the Hole [Figure 2 in A Templeton et al., 2021]. The early measurements of Eh, pH, temperature and pressure yielded a 1090 calculated fO₂ with a relatively smooth gradient, gradually declining with increasing depth. As for 1091 BA1B, BA3A and BA4A were also logged just once, within a few months of drilling. In BA3A, a pH log 1092 1093 two years after drilling revealed a small increase in pH throughout the hole, to ~ 11, suggestive of 1094 buffering involving Ca²⁺ and OH [Barnes and O'Neil, 1969; Bruni et al., 2002; J A M Leong et al., 2021b; J A M Leong and Shock, 2020; Neal and Stanger, 1984; Paukert et al., 2012]. BA3A is 5 1095 meters from water monitoring well NSHQ14, drilled in 2004. Aside from a steep gradient in fO2 in the 1096 upper 50 meters of NSHQ14, the pH and fO₂ profiles in BA3A and NSHQ14 are similar, suggesting 1097 1098 that they are close to steady state. 1099

The maximum pH in BA4A, ~ 10, is lower than in BA3A and NSHQ14, suggestive of buffering by brucite-water equilibrium [*J A M Leong et al.*, 2021b; *J A M Leong and Shock*, 2020]. Hole BA2A was essentially dry during drilling. After drilling, the Hole was immediately filled with intermediate alkalinity water pumped from a pool in a nearby canyon. Within 40 days, the Hole had partially collapsed, and the pH had risen to more than 10, up to 11, throughout the remaining open hole. Logging 1 year later yielded pH ~ 11 throughout the ~ 120 m of open hole.



1108Figure 24: pH and log fO2 from downhole logging in MBO Holes, and Omani Water Ministry monitoring well1109NSHQ14. fO2 from measured Eh, pH, temperature and pressure. Black line illustrates fO2 below which H2O1110dissociates to form H2, calculated from measured temperature and pressure. Rectangles: approximate bounds of1111fO2 for selected sulfide -metal associations at 50 MPa from Figure 16. Blue: pentlandite, fO2 < ~ 10⁻⁸² bars;1112orange: native copper + chalcopyrite, $10^{-80} > fO2 > ~ 10^{-82}$ bars; black: awaruite, $fO2 < ~ 10^{-75}$ bars.

- 1114 fO_2 throughout Holes BA2A and BA3A, and below 50 meters depth in NSHQ14, appears to be limited 1115 by the reduction of H₂O to form H₂ together with ongoing reduction of remaining ferrous iron in 1116 serpentine and brucite (Section 4.8). No calculated fO₂ values fall below the H₂O-H₂ buffer at any 1117 depth (within the uncertainty of measurement).
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1119	4. Discussion
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1121	4.1 Reactive fractionation
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1123	Dunite samples in core from the MBO have systematically lower Mg#'s than harzburgites from the
1124	same Holes, but the two lithologies have similar contents of Ni, a compatible element during igneous
1125	crystal fractionation (Figure 25, left). Dunites in the MBO also have highly variable Ca# (molar
1126	CaO/(CaO + NaO _{0.5} , Figure 25, right), suggesting enrichment of incompatible elements like Na via
1127	igneous crystal fractionation. The juxtaposition of these characteristics, with high, nearly constant
1128	compatible element concentrations combined with highly variable incompatible element enrichments,
1129	is the signature of "reactive fractionation", in which cooling, olivine-saturated magma begins to
1130	crystallize in the uppermost mantle while reacting with residual peridotite. Compatible element
1131	concentrations and Mg# in the resulting magmas are "buffered" by diffusive interaction with, and
1132	recrystallization of Ni-rich, high Mg# mantle olivine, together with dissolution of high Mg# mantle
1133	pyroxene. Meanwhile, decreasing magma mass leads to accumulation of incompatible elements in
1134	the remaining liquids. These characteristics have been previously observed in dunites and "troctolites"
1135	(plagioclase-bearing lherzolites, sensu stricto) sampled via dredging and drilling along the mid-ocean
1136	ridges (Section 1.2). Based on these considerations, we infer that the large dunite body intersected by
1137	boreholes at Sites BA1, BA2 and BA4 was the locus of reactive fractionation of primitive magmas in
1138	the uppermost mantle beneath the spreading ridge that formed the crust of the Samail ophiolite.
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1140 Alternatively, one could ask whether the Mg#, Ni contents or Ca#'s of the dunites and harzburgites in the MBO have been modified by alteration. For example, it has been proposed that low Mg#'s and 1141 MgO/SiO₂ in some weathered peridotites are produced by preferential dissolution and export of MgO, 1142 1143 as discussed further in Section 4.3. However, because Mg#'s in these rocks are not correlated with MgO/SiO₂ ratios, we do not think that the lower Mg#'s in dunites compared to harzburgites are the 1144 result of preferential MgO removal from the dunites. It is likely that Na has been removed from some 1145 igneous rock compositions via dissolution in reacting fluids (Section 4.2). However, this would serve 1146 to decrease the variation in Ca#, so that we don't think this process has been important in producing 1147 the highly variable Ca# observed in the MBO dunites. 1148

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Figure 25: Molar Mg# (Mg/(Mg+FeT)) versus Ni concentration (left) and molar Ca# (Ca/(Ca+Na)) in bulk compositions of dunite and harzburgite from MBO core, together with lower crustal gabbros from OmanDP Holes GT1A and GT2A, and compiled data on Samail ophiolite mantle samples ("Oman peridotites. Yellow field in the left panel outlines bulk rock compositions of harzburgites, dunites and "troctolites" sampled by drilling at 14-16°N the Mid-Atlantic Ridge on ODP Leg 209 [Kelemen et al., 2007; Seyler et al., 2007; Suhr et al., 2008]. Yellow field

in the right panel is for bulk compositions of peridotites dredged from mid-ocean ridges, calculated by Collier and 1157 1158 Kelemen [Collier and Kelemen, 2010] using data from Bodinier and Godard [J-L Bodinier and Godard, 2003], Niu 1159 [2004] and Tartarotti et al. [2002]. Figures modified from Figure F51 (left) and F54 (right) in Kelemen et al. [Kelemen et al., 2021g]. 1160 1161 4.2 Gabbroic dike compositions 1162 1163 1164 Based on the observations and interpretations of the shipboard science team, the protoliths of 1165 igneous dikes in core from the MBO appear to have been dominantly wehrlites, clinopyroxenites, olivine gabbros and gabbros [Kelemen et al., 2021d; f; g], rather than websterites and gabbronorites. 1166 The latter suite of orthopyroxene-rich rocks forms abundant dikes and small intrusions into the 1167 shallow mantle elsewhere in the Wadi Tayin and Samail massifs and is abundant in the northern 1168 massifs of the ophiolite (Section 1.3). In this interpretation, the dikes in MBO peridotites are similar to 1169 1170 those near the center of the "mantle diapir" inferred to be preserved in the Samail massif, and different from the orthopyroxene-rich dikes that are present in the mantle surrounding the "diapir" 1171 [Ceuleneer et al., 1996]. 1172 1173 However, interpretation of the MBO dikes in terms of igneous rock compositions should be 1174 1175 undertaken with caution. We computed CIPW norms for the bulk compositions of the 40 "gabbro" and 1176 "pyroxenite" dikes in MBO core that were analyzed by the shipboard team. In calculating the norms 1177 we assumed that all Fe is FeO for simplicity, and because the science team did not emphasize the 1178 presence of relict ferric-iron-bearing oxides in the dikes, perhaps because they are not present. 1179 1180 Most of the dike compositions are distinct from those of common gabbroic and ultramafic, igneous rocks. 65% of the compositions are peralkaline, with normative nepheline, leucite and/or kalsilite. Two 1181 peralkaline samples also contain corundum in the norm. All but two of the 14 samples that are not 1182 peralkaline contain normative orthopyroxene, which raises the question of whether alteration of the 1183 other dikes has removed a lot of SiO₂. Perhaps (some of) the protoliths were gabbronorites and 1184 1185 websterites, after all? 1186 Moreover, 60% of the norms contain more than 50% olivine, whereas gabbroic dikes and intrusions 1187 commonly contain approximately cotectic proportions of olivine and plagioclase, ± calcic pyroxene, 1188 with less than 30% olivine. On the other hand, ultramafic dikes commonly contain no plagioclase at 1189 all. Again, the presence of > 50% olivine in most of the CIPW norms for "gabbroic" dikes may be 1190 indicative of SiO₂ removal during alteration, rather than a record of the proportion of olivine present in 1191 1192 the igneous protolith of these rock compositions, which have been very substantially modified during alteration. 1193 1194 Finally, the CIPW norms consistently have high molar anorthite contents (An) in normative 1195 1196 plagioclase. All have normative An in plagioclase greater than 90%, all but one have normative An > 1197 95%, and 78% have An of 100%. In contrast, igneous plagioclase with more than 90% An is rare, and igneous plagioclase with 100% An is never observed in fresh igneous rocks [Kohut and Nielsen. 1198 2003]. Thus, it seems likely that Na has been removed from these rock compositions during 1199 1200 alteration. 1201 4.3 Pervasive silica addition to peridotites 1202 1203 1204 Figure 26 illustrates the compositions of MBO dunites and harzburgites in terms of wt% Al₂O₃/SiO₂ 1205 versus wt% MgO/SiO₂. For brevity, throughout the rest of this section, we will refer to these ratios as 1206 Al/Si and Mg/Si. This commonly used diagram was first used by Jagoutz et al. to infer the composition of the bulk silicate Earth [Jagoutz et al., 1979]. Such diagrams consistently show that partially 1207 serpentinized harzburgites and lherzolites have low Mg/Si at a given Al/Si ratio, compared to the 1208 1209 residues of partial melting and melt extraction in the upper mantle. Dunites, of course, have higher Mg/Si than harzburgites. Mixtures of high Mg# olivine and AI-bearing spinel in dunites have high, 1210

nearly constant Mg/Si over a large range of Al/Si, forming a nearly horizontal array on such diagrams.
 Again, partially serpentinized dunites commonly have Mg/Si lower than for the high Mg#, high Mg/Si
 protolith.



 1255
 fresh_dunite_wt%_MgO/SiO2 ~ 0.30 * observed_wt%_Al2O3/SiO2 + 1.21
 (10)

 1257
 assuming spinel-free dunites have Mg/Si of 1.21 (as in many of our dunite samples at low Al/Si), and
 spinels in dunites contain ~ 50 mole % MgAl2O4 and 50 mole % FeCr2O4, as is typical.

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 Supplementary Figure S14 demonstrates that the Mg/Si deficits, estimated in this way, are not

correlated with Mg# in dunites or peridotites, nor are they correlated with depth below the surface. 1262 Thus, though small amounts of Mg removal may have occurred, it is likely that the pervasively low 1263 Mg/Si in MBO harzburgites and dunites has been produced mainly by SiO₂ addition. In particular, 1264 many workers have proposed that serpentine can form, in part, via addition of dissolved SiO₂ to 1265 brucite, in general [Bach et al., 2004; Bach et al., 2006; J.S. Beard et al., 2009; Frost et al., 2013; 1266 1267 Klein and Bach, 2009; Klein et al., 2009; B.M. Tutolo et al., 2018] and related to specific observations in the MBO [Ellison et al., 2021; L.E. Mayhew et al., 2018; Miller et al., 2016; A Templeton et al., 1268 2021; A S Templeton and Ellison, 2020]. Evaluating the likely effect of water/rock reaction, using 1269 observed fluid compositions from the MBO and elsewhere in Oman, provides substantial support for 1270 1271 the SiO₂ addition hypothesis. Because fluids from peridotite-hosted springs and boreholes in the 1272 Samail ophiolite contain appreciable dissolved SiO₂, in all cases the reaction

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brucite $(3Mg(OH)_2) + 2SiO_2(aq) = chrysotile serpentine (Mg_3Si_2O_5(OH)_4) + H_2O$ (11)

is predicted to proceed from left to right, consuming brucite, adding SiO₂ to the rock, and producing
 serpentine (Supplementary Figure S2). As noted above, fO₂ calculated from Eh, pH, temperature and
 pressure in some deep borehole waters is very low, closely approaching the limit where H₂O is
 reduced to form H₂. However, in the presence of fluids with appreciable dissolved SiO₂, even these
 low fO₂ conditions favor oxidation of the Fe component in brucite, to form ferric-iron-bearing
 serpentine via

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1283 Fe-brucite $(4Fe^{2+}(OH)_2) + SiO_{2(aq)} = cronstedtite serpentine (Fe^{2+}_2Fe^{3+}SiFe^{3+}O_5(OH)_4) + H_2O + H_2 (12)$ 1284

1285 as quantitatively illustrated in Supplementary Figure S2, together with

1287 Fe-brucite $(5Fe^{2+}(OH)_2) + Fe^{2+}$ serpentine $(Fe^{2+}_3Si_2O_5(OH)_4) = 2Fe^{2+}_2Fe^{3+}SiFe^{3+}O_5(OH)_4 + H_2O + 2H_2.(13)$ 1288

The bulk compositions of almost all dunites and harzburgites in the MBO still retain molar (Mg+Fe²⁺)/Si ratios greater than 1.5 (for example, wt% MgO/SiO₂ greater than ~ 0.9 for a sample with molar Mg/(Mg+ Fe^{2+}) = 0.9), and thus they require the presence of brucite or cronstedtite as well as serpentine in fully hydrated normative mineral proportions. However, almost all of these calculated, fully hydrated mineral paragenesis are metastable with respect to the observed fluid compositions in peridotite-hosted springs and boreholes, which contain appreciable dissolved SiO₂. As a result, ongoing, gradual silica addition will continue to shift Mg/Si to lower values over time.

1297 The question arises, if brucite is a common phase throughout most of the core, yet most or all 1298 borehole waters contain dissolved SiO₂ concentrations higher than fluids in equilibrium with brucite, what is the source of the SiO₂? Bach et al. [2004] and Frost et al. [2013] suggested that SiO₂ for 1299 conversion of brucite to serpentine could be derived from alteration of orthopyroxene. However, while 1300 1301 this silica source may contribute in some parts of the system, many of the cores from the MBO are so 1302 highly serpentinized that they contain no relict pyroxene. Paulick et al. [2006] suggested that 1303 silicification of peridotites at ODP Site 1268 involved fluids derived from relatively SiO2-rich gabbroic rocks, but the proportion of gabbroic lithologies in the MBO is too limited to explain the widespread 1304 presence of relatively SiO₂-rich groundwater in altered peridotites. Similarly, one might consider that 1305 SiO_2 is derived from the continental crust and shelf sediments that underlie the Samail ophiolite. 1306 1307 However, low Sr isotope ratios in altered peridotites rule out a continental component in fluids during 1308 weathering [Supplementary Figure S3 and related text in Kelemen et al., 2011], except in specific locations just above the basal thrust beneath the ophiolite [Kelemen et al., 2021]] and just below the 1309 Cretaceous unconformity above the ophiolite [de Obeso and Kelemen, 2018]. 1310 1311

1312 Other suggestions regarding the source of SiO₂ for silicification of brucite involve weathering reactions 1313 within the serpentinites themselves. Thus, Klein et al. [2009] and Beard et al. [*J.S. Beard et al.*, 2009] 1314 invoked silica dissolution during oxidation of Fe^{2+} from serpentine to form magnetite via

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1316	$Fe_3Si_2O_5(OH)_4 = Fe_3O_4 + 2SiO_2(aq) + H_2O + H_2.$	(14)
1317		

On the one hand, this kind of reaction might not be an important source of SiO₂ in the MBO, since 1318 many investigators have concluded that formation of magnetite during oxidative, hydrous alteration of 1319 1320 peridotite is uncommon below ~ 200°C [e.g., Klein et al., 2014; Klein et al., 2009; McCollom and Bach, 2009; McCollom et al., 2016; Streit et al., 2012]. On the other hand, however, whole core 1321 magnetic susceptibility data [Kelemen et al., 2021d; f; g; A Templeton et al., 2021] indicate an 1322 average abundance of less than 1.5 wt% magnetite throughout most of the core [e.g, Figure 1 and 1323 related calculations in Ellison et al., 2021]. Alternatively, Streit et al. [2012] and Ellison et al. [2021] 1324 suggested that dissolved SiO₂ rises due to carbonation reactions such as 1325 1326

1327 1328

$$Mg_{3}Si_{2}O_{5}(OH)_{4} + 3CO_{2} = 3MgCO_{3} + 2SiO_{2}(aq) + 2H_{2}O.$$
 (15)

Formation of Mg-carbonate minerals by reaction of dissolved CO₂ with peridotite certainly does 1329 1330 increase SiO₂ activity, driving up the Si/Mg ratio in silicate minerals [e.g., Falk and Kelemen, 2015; 1331 Frost, 1985; Kelemen et al., 2011; Klein and Garrido, 2011; Streit et al., 2012], and indeed, veins in 1332 core record Mg-carbonate formation in the shallow portions of Holes BA1B, BA3A and BA4A [Section 3.3 and Kelemen et al., 2021d; f; g]. However, it remains unclear to us whether the proportion and 1333 rate of carbonation in the uppermost part of the peridotite-hosted aquifer is sufficient to overcome the 1334 buffering capacity of brucite-bearing serpentines and produce the relatively high SiO₂ contents 1335 observed in almost all borehole water samples. 1336

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1338 In any case, mass balance requires the continued presence of brucite in fully hydrated MBO dunite 1339 and harzburgite compositions (Figure 9 and related calculations). In keeping with these calculations, 1340 brucite is observed in the MBO core. For example, although sampling for X-ray diffraction onboard DV 1341 Chikyu was commonly focused on identifying relatively coarse-grained minerals in veins, shipboard Xray diffraction data for serpentine-bearing samples detected the presence of brucite in 10 to 15% of 1342 analyzed samples, while less biased, electron microprobe, X-Ray diffraction and Raman analyses 1343 revealed the presence of brucite in a significant proportion of samples in drill cuttings from rotary 1344 1345 boreholes NSHQ14, BA1A and BA2A [Kelemen et al., 2021d; e; L.E. Mayhew et al., 2018; Miller et 1346 al., 2016]. Finally, 6 of 11 samples from Hole BA3A, 13 of 15 samples from Hole BA4A, and 21 of 23 1347 samples from Hole BA1B analyzed by quantitative XRD contained appreciable brucite [Ellison et al., 1348 2021] [A Templeton et al., 2021].

In this context, the presence of brucite in the mesh-textured, serpentinite matrix is similar to the
presence of highly reduced sulfides in cores from shallow depths in the MBO. While equilibrium may
be closely approached at the micro- to nano-scale in these samples, it is likely that mesh cores are far
from equilibrium with fluids in nearby fractures that are similar to spring and borehole waters.

4.4 Correlation of water properties and core composition

1356 1357 The shipboard science team quickly realized that there is a strong correlation between carbonate vein 1358 abundance and pH in borehole waters, in data from Holes BA1B and BA4A (Figure 27, left; BA1B log vein frequency per 25 m = 11.9 - 1.056 x - pH, $R^2 = 0.90$; BA4A, log vein frequency per 25 m = 1359 17.443 – 1.68 x pH, R² = 0.92). Indeed, interpreting C concentration and ¹⁴C data for peridotite hosted 1360 1361 carbonate veins and travertines in the Samail ophiolite, Kelemen and Matter [Kelemen and Matter, 1362 2008] inferred the presence of a shallow horizon of carbonate vein deposition just beneath the 1363 surface, with most carbonate veins in a ~ 15 m layer below the present-day erosional surface. This relationship is not as clear in data from Hole BA3A, where a fault at ~ 70 m depth is associated with a 1364 peak in carbonate vein frequency. Consistent with the observed correlation in BA1B and BA4A, less 1365 comprehensive observations of carbon concentration in core samples show a correlation between the 1366 1367 pH of borehole water and the carbon content of core from Hole BA1B (Figure 27, right).

Since the solubility of dissolved carbon species decreases rapidly with increasing pH, the shipboard team attributed the correlation of carbonate vein abundance with depth to carbonate precipitation as pH increased along a reaction path, as water descending through the porous aquifer interacts with increasing amounts of peridotite. This seems evident, even obvious... except that it does not explain the correlation between present-day fluid compositions and carbonate abundance, unless the
1374 carbonate veins are also young, precipitated from descending fluids near the present-day erosional1375 surface.

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As for borehole pH and the carbon content of core, since both the ferric to ferrous iron ratio in core samples and the oxygen fugacity in borehole waters systematically decline with increasing depth in Hole BA1B, one might expect a correlation between borehole water fO_2 and whole rock Fe^{3+}/Fe^{2+} . As shown in Figure 27, center, this correlation may be present, though it is not very strong.



¹³⁸² 1383

Figure 27: Relationships of core observations to water compositions in boreholes at the same depth. The log of carbonate vein frequency (25 m running average) in Holes BA1B and BA4A decreases with increasing pH in borehole fluids. Ferric to total iron ratios in core from Hole BA1B are weakly correlated with fO₂ in borehole water from the same depth. CO₂ content in core from Hole BA1B is high at relatively low pH, while it is low and less variable at high pH in borehole waters. [Data from this paper and Kelemen et al., 2021d; g]

Carbonates in core from the MBO are generally in veins within fractures, which are macroscopic conduits for fluid flow and probably record high time-integrated water/rock ratios. Thus, one might expect a reasonably strong correlation between carbonate mineral abundance in core, and the composition of water in larger fractures, and in boreholes that are filled primarily by flow in larger fractures.

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Figure 28: Maximum log fO_2 at which various mineral assemblages, individual minerals and metals are stable at 35°C and ~ 1 to 500 bars (see Figure 16) versus fO_2 in borehole water at the depth at which these minerals were observed in MBO core. Circles: BA1B. Squares BA3A. Diamonds: BA4A. Data compiled from shipboard optical petrography and XRD observations [Kelemen et al., 2021d; f; g]. 1398 In contrast, nickel-, copper- and iron-bearing minerals are found throughout our rock samples, in 1399 mesh cores as well as veins. These different micro-environments record very different oxidation 1400 states which could all be present in peridotite-hosted aguifers at the same time, juxtaposed on very short length scales. For example, as emphasized by de Obeso and Kelemen [2020], some peridotite 1401 outcrops elsewhere in the Samail ophiolite preserve almost the entire range of fO₂ on Earth, over a 1402 1403 length scale ~ 10 cm, from native metals and highly reduced sulfides in dark serpentinites to rusty orange, clay-bearing assemblages in which all iron is ferric. 1404

1405 Similarly, as noted in Section 3.2, Kelemen et al. [2021d; f; g] and Eslami et al. [Eslami et al., 2018], 1406 awaruite, native copper, heazlewoodite, pentlandite and magentite are found - in various 1407 combinations - in the serpentinite matrix of samples from a range of depths, and a corresponding 1408 1409 range of fO_2 in borehole waters logged at the same depth (Figure 28).

1410 1411

4.5 Sulfur-rich. "black serpentinite" zone from 30-150 m depth in Hole BA1B

1412 1413 The relatively high sulfur content, up to 0.6 wt% of the BA1B core in some samples located between ~ 1414 30 and 150 meters depth (Figure 12) – almost certainly in microscopic Ni sulfide together with sulfide-1415 hydroxide±carbonate minerals such as tochilinite and haapalite (Section 2.6) – suggests another potential correlation between the mineralogy of the core and present-day borehole fluid compositions. 1416 Sulfur concentrations in the core in this interval [Kelemen et al., 2021d] are 10 to 100 times higher 1417 than in samples from outcrops of less weathered, residual mantle dunites and harzburgites from other 1418 parts of the Samail ophiolite (5 to 100 ppm in 21 samples from Hanghoj et al. [2010], 100 to 500 ppm 1419 1420 in 5 samples from Oeser et al. [2012]. This observation, coupled with the weathering-related redox gradients in the MBO – recorded by the decline in Fe³⁺/(total Fe) ratios with depth in core 1421 1422 compositions, and by declining fO_2 with depth in borehole waters – calls to mind well-known enrichments of Ni in laterites, and copper in supergene deposits (e.g., 1423

https://en.wikipedia.org/wiki/Supergene). These are generally thought to form via dissolution of metals 1424 in oxidized, near-surface ground waters, and re-precipitation of those components at greater depth, 1425 as downward migrating fluids become reduced by reaction with surrounding rocks. 1426 1427

1428 Indeed, protracted, Late Cretaceous sub-aerial weathering of peridotite elsewhere in Oman formed 1429 laterite deposits [S AI Khirbash, 2015; S A AI Khirbash, 2016; 2020]. It could be that the enriched 1430 sulfur horizon from ~ 30 to 150 m depth in BA1B core contains sulfur that was originally leached from 1431 rocks above the current erosional surface, that have since eroded away. Indeed, this seems likely, since a simple interpretation of this process would require accumulation of sulfur leached from a 1432 volume of weathered peridotite that was 10 to 100 times larger than the volume of sulfur-enriched 1433 1434 peridotite sampled by the core.

1435 On the other hand, we hypothesize that this chromatographic process, with oxidative dissolution of 1436 sulfur from near surface rocks coupled with deeper sulfate reduction and sulfide precipitation, is 1437 ongoing. As emphasized by Templeton et al. [A Templeton et al., 2021], during drilling of Hole BA1B, 1438 large quantities of "black goo", stinking of H_2S , were suddenly produced with the core at a depth of 1439 about 30 meters. Templeton et al. [A Templeton et al., 2021] report that XRD data on the "black goo", 1440 from this depth, and also from a fault zone at 70 meters depth, contain a peak at 16° 2-theta, that 1441 could correspond to the primary peak for tochilinite. A likely interpretation of the data on sulfide 1442 concentration in the core, the "black serpentinite" zone in the core, and the presence of stinky black 1443 1444 goo possibly containing tochilinite, is that there is ongoing sufur reduction and sulfide precipitation in 1445 this depth range, fed by sulfate-bearing fluids descending from shallower depths, where fluids leach of 1446 sulfur from a shallow, oxidative weathering horizon.

1447 In 2018, a few months after drilling, fO₂ in BA1B borehole waters at 30 to 150 m depth was ~ 10^{-30} to 1448 1449 10^{-40} bars, too high for sulfide saturation at the low dissolved sulfur concentrations we model ($\Sigma S < 10^{-10}$ ³ molal, Figure 29). As noted in Section 3.5, because drilling operations used fresh, oxidized drinking 1450 water for lubrication, it may be that steady state fO2 at these depths had not yet been attained when 1451 the Hole was logged. *In any case*, thermodynamic modeling, presented in Section 4.6, shows that 1452 fO_2 drops from ~ 10⁻³⁵ bars to 10⁻⁶⁵ bars – where sulfide saturation is predicted in our Step 2 models 1453 illustrated in Figure 29 - over a very short interval of reaction progress. Thus, a small increment of 1454 reaction between borehole waters and surrounding rocks would lead to sulfide precipitation. 1455 1456

1457 *More generally*, borehole waters may record ambient fluid compositions in large fracture systems, 1458 which are probably the locus of most fluid flow in the peridotite-hosted aquifer. Thus, prior to drilling, relatively oxidized waters with fO₂ from 10⁻³⁰ to 10⁻⁴⁰ bars may have already been present in the larger 1459 fracture systems at 30 to 150 m depth. However, where these waters infiltrate smaller fracture 1460 systems, and/or react diffusively with surrounding rocks, it is likely that they become highly reduced 1461 1462 and sulfide-saturated, contributing to continued accumulation of sulfide minerals in the black serpentinite zone. In this scenario, over time the erosional surface will continue to migrate downward 1463 with respect to the present-day surface, and the supergene enrichment zone will also migrate 1464 1465 downward, as sulfides at the top of the zone are gradually oxidized by near surface fluids, and begin to dissolve. In this way, such zones can be both ancient, and active. 1466

1467

1468 It has been proposed that the formation of supergene metal enrichment, via low temperature sulfide 1469 precipitation, is unlikely without the intervention of sulfate-reducing bacteria [e.g., Tornos et al., 2019: 1470 Zammit et al., 2015]. In turn, Templeton et al. [A Templeton et al., 2021] report that sulfate-reducing microbial activity has not yet been detected in extracts from BA1B core samples in the 30 to 150 1471 1472 meter black serpentinite zone. In contrast, extracts from core retrieved from greater depth, where 1473 borehole waters record more reducing conditions, show evidence of biological sulfate reduction in the 1474 lab. The maximum rates of microbial sulfate reduction occurred in samples from 280 m depth, where fO_2 in borehole water was ~ 10^{-62} bars in 2018. 1475

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On the basis of these observations, one hypothesis might be that microbial reduction of sulfate at ~ 1477 250 to 300 m depths produces H_2S , which then migrates **upward** through the rocks – perhaps along 1478 1479 fault zones at 30 and 160 meters depth - to produce the observed sulfur enrichment in rocks at 30 to 1480 150 m depth. However, here we suggest a simple alternative, that supergene sulfur enrichment is 1481 ongoing, with *descending*, oxidized, near-surface fluids dissolving sulfur from the oxidized red zone 1482 from 0 to 30 m depth, and transporting dissolved sulfate downward. This continues until the fluids become reduced by reaction with serpentinites, and precipitate sulfides in the black serpentinite zone 1483 from 30 to 150 meters depth. In this alternative interpretation, either microbial activity is not essential 1484 to this process, or the microbes that facilitate this relatively shallow process have not yet been 1485 detected in samples extracted from core. Indeed, in water samples from obtained from the 41 to 132 1486 1487 m depth interval of Hole BA1A via packer sampling, Nothaft et al. [2021a] found that 20 to 92% of 16S 1488 rRNA gene amplicon sequences were affiliated with a class of bacteria supported by sulfate 1489 reduction.

4.6 Reaction path modeling including Cu, Ni and S

1492 1493 In order to quantify the hypothesis that the black serpentine zone observed in BA1B core may form via supergene enrichment, we conducted geochemical reaction path modeling, using methods 1494 described in detail in Section 2.5. We followed the general rubric outlined by Barnes and O'Neil 1495 [Barnes and O'Neil, 1969] and Neal and Stanger [Neal and Stanger, 1985], and modeled by Bruni et 1496 al. [Bruni et al., 2002], Paukert et al. [Paukert et al., 2012] and Leong et al. [J A M Leong et al., 1497 2021b]. In these models, rainwater falling on peridotite dissolves Mg²⁺ and other components from the 1498 rock, charge balanced mainly by uptake of CO₂ from air to form HCO₃-. This process forms Mg-HCO₃-1499 1500 rich waters with pH ~ 8.5 to 10, which Barnes and O'Neil termed Type I. As extensively discussed elsewhere [e.g., Kelemen et al., 2011 and references therein], Type I waters in the Samail ophiolite 1501 are typically sampled from wadis (small canyons) and shallow groundwater wells in the peridotite-1502 1503 hosted aquifer. Some Type I fluids are then thought to continue reacting with peridotite at greater 1504 depth, isolated from the atmosphere. Precipitation of serpentine and Mg-bearing carbonates along 1505 this reaction path, together with dissolution of Ca-bearing phases, produces low Mg and C, Ca-OH rich fluids with pH > 10 and low fO_2 , which Barnes and O'Neil termed Type II waters. In all of these 1506 respects, our new models do not depart significantly from past results. 1507

1508 1509 However, our new models incorporate dissolved S, Ni and Cu, together with a host of metal and sulfide minerals, and thus can be used to evaluate potential mechanisms of supergene sulfide 1510 enrichment in the serpentinized peridotites hosting Hole BA1B. The results of these models are 1511 depicted in Figure 29. As predicted on qualitative grounds, formation of Type I fluids via reaction open 1512 to CO₂-uptake from air is accompanied by dissolution of sulfur-bearing phases. In turn, reaction of 1513 Type I fluids with serpentinite, closed to CO₂ uptake from air, leads to precipitation of serpentine, 1514 dolomite and hematite, together with production of highly reduced fluids that precipitate sulfides and 1515 1516 native metals. When dissolved O₂ concentrations drop below those of dissolved H₂, a dramatic drop in 1517 fO_2 from 10^{-35} to 10^{-65} bars over a narrow range of water rock ratios ($10^{3.391195}$ to $10^{3.390982}$). This is 1518 accompanied by saturation in native copper and sulfide minerals cubanite, millerite and pyrite. As fO_2 1519 continues to fall, and sulfide precipitation also lowers fS_2 , hematite precipitation is supplanted by 1520 magnetite, there is another big drop in fO_2 over a narrow range of reaction progress, overall sulfide 1521 precipitation declines, and the sulfide and metal assemblages associated with magnetite that have 1522 been observed in serpentinite mesh cores (Section 3.2) – heazlewoodite, chalcopyrite, and ultimately 1523 awaruite – are predicted to form.





1525 1526

Figure 29: Results of thermodynamic reaction path modeling at 35°C and 50 MPa. From the perspective of fluid
gradually reacting with rock, reaction progress increases from right to left, as the water/rock ratio (W/R)
decreases.

1530 Because the Klein et al. [2013] thermodynamic database used for this modeling (Section 2.5) is limited 1531 to 50 MPa, these results for 50 MPa, whereas the maximum pressure in MBO boreholes is \sim 4 MPa. Fortunately, 1532 few relevant equilibria (other than H₂ saturation in water!) are dependent on pressure in this range.,

1533Results are presented in terms of abundance of precipitated minerals (top row) and dissolved species1534(bottom row). Bottom right panel also illustrates fO2 (red line), fO2 values at the H2O-H2 limit where water1535breaks down to form H2 (horizontal, dashed red lines), and corresponding dissolved H2 concentrations at H2-gas1536saturation (horizontal, dashed grey lines) at 0.1, 0.4, 20 and 50 MPa.

1537 Step 1 (lefthand panels) simulates reaction of rainwater with peridotite, in a system in equilibrium with
1538 air. Step 2 (righthand panels) simulates reaction between water produced in step 1 and serpentinized peridotite,
1539 in a system isolated from air. Step 1 produces oxidized, clay- and hematite-bearing serpentinites (upper left
1540 panel) while dissolving sulfur from the protolith, and solute-rich fluids with pH ~ 8 and ~ 1 millimole dissolved

sulfur (lower left). Step 2 produces reduced serpentinites with magnetite, sulfides, and metal alloy (upper right),
 together with sulfur-, magnesium-, silicon- and carbon-poor fluids (lower right).

1543 A sharp sulfide precipitation front accompanies a drop in fO_2 from ~ 10⁻³⁵ to 10⁻⁶⁵ bars at a water/rock 1544 mass ratio ~ 10^{3.39}. Illustrating this, the middle panel on right illustrates sulfur concentration in precipitated solids 1545 at a given water/rock ratio (black line). This forms a sulfur-rich zone at water/rock ratios from ~ 10^{3.3} to 10, similar 1546 in origin to supergene sulfide deposits.

The middle panel also illustrates results in terms of iron redox (orange lines). Cumulative $Fe^{3+}/(total Fe)$ 1547 in all precipitated solids is illustrated with small dashes, cumulative moles Fe precipitated are shown with the 1548 1549 solid line, and cumulative moles of Fe³⁺ precipitated are tracked with large dashes. Because this reaction path model includes solid solutions, whereas the calculations in Figure 31 are for pure mineral end-members, the 1550 1551 results in the middle panel provide a crucial complement to those in Figure 31, for understanding the evolution of fO2. Although Fe3+/(Fe total) of precipitating solids declines with reaction progress at a water/rock ratio less than 1552 $\sim 10^2$, it only falls by a factor of ten in the buik, and a factor of five in the serpentine (Supplementary Figure 15), 1553 1554 whereas the amount of precipitated solids (mostly brucite + serpentine) increases by a factor of ~ 100 from water/rock of 10² to 10^{-0.8}. In this model at 50 MPa, H₂ partial pressure is not limited to 4 MPa, (dissolved H₂ ~ 30 1555 mM) but instead increases to 50 MPa saturation (water/rock ~ 10^{-0.8}, ~ 375 mM dissolved H₂). In the MBO system 1556 1557 at ~ 4 MPa, dissolved H₂ concentration would be limited to ~ 30 mM, fO₂ would be fixed at about 10⁻⁸⁰ bars, and H_2 gas would evolve with continued oxidation of Fe^{2+} in the protolith to form increasingly large cumulative masses 1558 1559 of Fe³⁺-bearing serpentine.

Abbreviations: Serpentine (Srp, chrysotile + greenalite + Fe²⁺-cronstedtite solid solution), talc (Tlc, talc 1560 + minnesotaite solid solution), Mg-saponite (Sap), Mg-amesite (Ame), garnet (Grt, andradite + grossular solid 1561 1562 solution), magnesite (Mgs), calcite (Cal), dolomite (Dol), gibbsite (Gbs), hematite (Hem), brucite (Brc, Mg and Fe²⁺ solid solution), magnetite (Mag), tenorite (Tnr), millerite (MIr), cubanite (Cbn), pentlandtite (Pn), 1563 heazlewoodite (Hzl), pyrite (Py), native copper (Cu), native nickel (Ni), and awaruite (Awr). Amesite is treated as 1564 an end-member phase, not part of the serpentine solid solution. In natural rocks, amesite is a component in 1565 1566 serpentine solid solutions. Similarly, native Ni and awaruite (Ni₃Fe) are treated as end-member phases in the 1567 calculation, whereas in some studies a range of Fe/Ni ratios has been observed ...

1568 1569 Some potentially significant departures of model results from observations include saturation in 1570 millerite, cubanite and pyrite, which haven't been observed in the core, and precipitation of Ni metal from W/R ~ 100 to 10, prior to formation of awaruite. The latter discrepancy is perhaps explained by 1571 the fact that the method used for modeling cannot account for solid solutions. Frost [1985] and Sleep 1572 1573 et al. [2004] noted that if there were complete solid solution from Ni to Fe metal, one might use the 1574 Fe/Ni ratio as an indicator of fO₂. In essence, because Ni-NiO occurs at much higher fO₂ than Fe-1575 FeO, one could anticipate a negative correlation between oxygen fugacity and the Fe content of NiFe 1576 alloys. Low temperature phase equilibria in this system are uncertain [Cacciamani et al., 2010; Howald, 2003; Klein and Bach, 2009; Navak and Meyer, 2015]. Fe-rich "taenite", "awaruite" and 1577 "tetrataenite" are reported in terrestrial serpentinites [Botto and Morrison, 1976; Navak and Meyer, 1578 2015], while Sciortino et al. [2015] and Ellison et al. [2021] analyzed "awaruite" with low Fe contents in 1579 serpentinites, including in a sample from 100 m depth in Hole BA3A. Similarly, incomplete 1580 1581 observations, and/or lack of solid solution data in the thermodynamic calculations, may be responsible for model predictions of sulfides that have not (yet?) been observed in core, and conversely for the 1582 1583 lack of model predictions of sulfides that are observed. 1584

Overall, solid reaction products are predicted to have high total sulfur contents in the range of water 1585 rock ratios from 10^3 to 10^1 , which we propose is the mechanism for the formation of the sulfur-rich. 1586 black serpentinite zone from ~ 30 to 150 m depth in BA1B core. More generally, the model whose 1587 results are depicted in Figure 29, and other, similar, previous models of the evolution of Type I and 1588 Type II fluids in peridotite-hosted aquifers, include the implicit assumption that all of the reactions 1589 1590 involved are ongoing, perhaps even at steady state. Of course, this assumption is approximate, and it 1591 is likely that the rocks contain armored relicts of earlier mantle and alteration phase assemblages. With that said, specific instances of apparent disequilibrium, relict mantle minerals, or "out of 1592 sequence" alteration assemblages may be preserved relicts of prior events, but they could also be 1593 1594 indicative of micro to meter scale variation in fluid/rock ratios in a reactive system that is close to equilibrium at small length scales, over times of tens to hundreds of thousands of years. 1595

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4.7 Rate of ongoing alteration

The ¹⁴C data for carbonate veins (Section 3.4, Supplementary Table 3), together with the fact that
texturally young, waxy serpentine veins are intergrown with, and locally crosscut, young carbonate
veins, indicates that serpentine formation occurred in the Pleistocene and probably continued in the
Holocene. Together, waxy serpentine abundances ~ 5 volume percent, and measurable ¹⁴C "ages" of
20 to 50 kyrs for 2/3 of the carbonate samples analyzed, yield an order of magnitude estimate of ~ 1

vol% serpentine formation per 10,000 years, equivalent to a volume fraction of 3 10⁻¹⁵/s. This estimate
is roughly consistent with new, experimentally-based estimates of low temperature serpentine
formation from olivine [*Lamadrid et al.*, 2021] and estimates of the Fe-redox rate based on observed
H₂ and CH₄ gas fluxes [*J A Leong et al.*, 2021a]. In keeping with other work and considerations in
Section 4.3, we hypothesize that most of the ongoing serpentine formation occurs via addition of
aqueous SiO₂ to brucite to form Mg-rich serpentine, and oxidation of Fe-brucite to form ferric-ironbearing serpentine.

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4.8 Controls on fO₂, pH and dissolved SiO₂ in borehole waters

Figure 30, left, shows that fO_2 in some boreholes very closely approaches the limit where H_2O is 1614 1615 reduced to form H₂ Also, much has been made of the observation of H₂-rich gases bubbling out of 1616 peridotite-hosted alkaline springs in the Samail ophiolite and elsewhere [e.g., Boulart et al., 2013; 1617 Neal and Stanger, 1985; Sano et al., 1993; Vacquand et al., 2018]. It is proposed that reactions between water and peridotite produce highly reduced fluids, which evolve free H₂ gas. Indeed, fO₂ in 1618 the lower parts of BA3A 2018, NSHQ14 2018, and BA2A appears to be fixed by a combination of the 1619 reaction $2H_2O = 2H_2 + O_2$ reaction itself, and some sink for O_2 at low fO_2 . Obviously, in the presence 1620 1621 of excess water, fO₂ cannot decline below the value fixed by this reaction at a given temperature and pressure. Conversely, the rocks still contain ~ 3 wt% ferrous iron (Figure 12). Since the average 1622 proportion of magnetite inferred from magnetic data is less than 1.5 wt%, and only 31 wt% of 1623 magnetite is composed of FeO (accounting for < 0.5 wt% FeO in bulk rocks), some ferrous iron must 1624 still reside in serpentine or brucite, as confirmed by X-ray and Raman spectroscopic analyses of 1625 1626 serpentine and brucite in BA3A core samples [Ellison et al., 2021].

1628 Ongoing oxidation of the remaining Fe^{2+} in serpentine and/or brucite, could provide a continuing sink 1629 for O₂, with concurrent production of H₂, thus pinning fO₂ at the H₂O-H₂ reaction limit. If this 1630 hypothesis is correct, and if we could obtain gas-tight samples of pore fluid from the rocks 1631 surrounding the bottoms of these Holes, we predict they would be H₂-saturated. We are not certain of 1632 the nature of the specific reactions that continue to consume O₂, and produce H₂, at the H₂O-H₂ limit. 1633 Magnetite is stable with respect to Fe-brucite, down to about 2 log units below H₂O-H₂ (Figure 31), so 1634 that brucite oxidation could play a role via

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$$6Fe^{2+}(OH)_2 + O_2 = 2Fe^{2+}Fe^{3+}_2O_4 + 6H_2O$$
(16)

1638 Similarly, remaining Fe^{2+} in serpentine (greenalite, cronstedtite) could be oxidized to form magnetite 1639 and/or cronstedtite via

1640 1641

 $2Fe^{2+}_{3}Si_{2}O_{5}(OH)_{4} + O_{2} = 2Fe^{2+}Fe^{3+}_{2}O_{4} + 4SiO_{2}(aq) + 4H_{2}O_{3}$ (17, also 14)

1642 1643

$$6Fe^{2+}{}_{2}Fe^{3+}SiFe^{3+}O_{5}(OH)_{4} + O_{2} = 8Fe^{2+}Fe^{3+}{}_{2}O_{4} + 6SiO_{2}(aq) + 12H_{2}O,$$
 (18)

1644
1645 and
$$8Fe^{2+}{}_{3}Si_{2}O_{5}(OH)_{4} + 3O_{2} = 6Fe^{2+}{}_{2}Fe^{3+}SiFe^{3+}O_{5}(OH)_{4} + 10SiO_{2}(aq) + 4H_{2}O.$$
 (19)

1646 1647 Reactions 16, 17 and 18 involve production of magnetite, and thus may be inconsistent with various observations and calculations indicating that magnetite production during peridotite alteration is 1648 limited at low temperature (Section 4.3). However, it may be that prior work has not fully explored the 1649 very low fO₂ conditions near the H₂O-H₂ limit at low temperature and pressure, and/or that the 1650 1651 thermodynamic data are uncertain. Note that the results of the reaction path model in Figure 29, 1652 incorporating solid solutions, include a small amount of magnetite precipitation at a water/rock ratio ~ 200, and a predicted increase in the total amount of Fe³⁺ incorporated in serpentine with reaction 1653 progress at water/rock less than 200, with fO₂ at the H₂O-H₂ fO₂ limit. In addition to providing an 1654 ongoing sink for O_2 (source of H_2) at the H_2O-H_2 limit, reactions 17-19, involving continued reduction of 1655 Fe²⁺ in serpentine, could also be providing a source of "excess" dissolved SiO₂ for brucite silicification 1656 1657 (Section 4.3). An additional potential O_2 sink in the MBO might be ongoing serpentinization of relict olivine, which is observed in less altered core samples, particularly in the lower part of Hole BA1B. 1658 This could include reactions such as favalite-greenalite-magnetite 1659 1660

1661 1662

$$12Fe^{2+}SiO_4 + 12H_2O + O_2 = 2Fe^{2+}Fe^{3+}O_4 + 6Fe^{2+}Si_2O_5(OH)_4$$
(20)

1663 and/or fayalite-greenalite-cronstedtite

$$5Fe^{2+}SiO_4 + 6H_2O + O_2 = Fe^{2+}Fe^{3+}SiFe^{3+}O_5(OH)_4 + 2Fe^{2+}Si_2O_5(OH)_4.$$
(21)

In contrast to the highly reduced water inferred from 2018 data for the deeper parts of Holes BA2A, 1667 BA3A and NSHQ14, fO₂ calculated from logging data for Holes BA1A and BA4A in 2018, and BA1D 1668 1669 in 2019 is higher, and appears to approach an asymptote at about 4 log units above the H₂O-H₂ limit toward the bottoms of these Holes. This might be explained by various proposed buffers for fO2 1670 involving awaruite, andradite, diopside and/or calcite [e.g., Ellison et al., 2021; Frost and Beard, 2007; 1671 J A Leong et al., 2021a]. However, Ni and Ca, are relatively minor components in the rocks, 1672 suggesting that equilibria involving these Ni- and Ca-bearing minerals may have limited buffer 1673 capacity. Instead, we suggest that equilibria involving Fe^{2+} -Mg solid solutions in cronstedtite 1674 $((Mg, Fe^{2+})_2 Fe^{3+} SiFe^{3+} O_5(OH)_4, chrysotile ((Mg, Fe^{2+})_3 Si_2 O_5(OH)_4), and brucite (Mg, Fe^{2+})(OH)_2 are$ 1675 buffering fO₂ in waters near the bottom of these Holes. Figure 31 illustrates the results of 1676 thermodynamic calculations illustrating that, depending on the Mg/Fe^{2+} content of the cronstedtite, 1677 these reactions constrain fO_2 to within 2.5 to 4.5 log units of the H₂O-H₂ reaction. If we consider only 1678 the Mg-cronstedtite endmember, then the fO_2 range is 3.5 to 4.5 log units above H_2O-H_2 , which in turn 1679 1680 is consistent with the apparent asymptotic fO₂ values for water at the bottom of Holes BA1A 2018, BA1D 2019 and BA4A 2018. The hypothesis that these brucite-serpentine mineral assemblages 1681 buffer fO2 in serpentinizing systems at depth is appealing, because these minerals are composed of 1682 the major elements present in the rocks. 1683 1684



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1687Figure 30: Compiled data on downhole variation in fO_2 (left) and pH (right) in MBO borehole waters. Red1688rectangle on left illustrates fO_2 for reduction of H_2O to form H_2 at ~ 35°C and 40 bars, \pm 1 log unit (likely1689precision of borehole fO_2 calculated from Eh, pH, temperature and pressure). Green rectangle in lefthand panel1690illustrates range of fO_2 buffered by reactions involving brucite, cronstedtite, and chrysotile-greenalite solid1691solutions. Green rectangle in righthand panel illustrates pH range for coexisting brucite, serpentine and1692andradite.

In addition, brucite-serpentine equilibria also have a potentially important control on dissolved SiO₂
 concentrations and pH in coexisting fluids. Mg-brucite-Mg-chrysotile and Mg-chrysotile-Mg-talc

equilibria constrain SiO₂ activity in fluids to range from 10^{-8.2} to 10^{-4.7}. This range of SiO₂ activities 1696 encompasses observed aSiO₂ in almost all peridotite-hosted borehole and alkaline spring water 1697 samples from the Samail ophiolte with pH > 9 [J A M Leong et al., 2021b]. In turn, Mg-brucite-Mg-1698 chrysotile equilibrium in this SiO₂ activity range constrains pH to be \geq 10. Mg-brucite and Mg-1699 chrysotile in combination with andradite, which is commonly intergrown with serpentine in core 1700 samples from the MBO [Ellison et al., 2021; Kelemen et al., 2021d; f; g; A Templeton et al., 2021], 1701 constrain pH to ≤ 11.5. Though pH in borehole waters increases downward near the top of most 1702 holes, it is variable at depth, and does not show the asymptotic patterns that are evident in the fO2 1703 data. However, with the exception of BA1A 2018, the range of pH in all borehole waters logged more 1704 than a year after drilling is 10 to 11.3, consistent with the hypothesis that brucite + serpentine ± 1705 andradite equilibria control fO₂ in the lower part of these boreholes. 1706 1707



1708

1709 Figure 31: Phase diagrams in terms of temperature vs log fO_2 (left) and log activity of dissolved SiO₂ vs log fO_2 1710 (right), for various reactions involving Mg- and Fe-brucite (Brc, FeBrc), Mg- and Fe²⁺-cronstedtite (MgCtd, Ctd), chrysotile (Ctl), greenalite (Gre), goethite (Gth), magnetite (Mag), awaruite (Awr), heazlewoodite (Hzl), bunsenite 1711 (Bun), andradite (Adr), fayalite (Fa) and hisingerite at 45°C and 4 MPa (T and P near the bottom of BA1A, BA1B 1712 and BA1D). Because of the choice of thermodynamic database, these results do not incorporate solid solutions. 1713 1714 In the right panel, the stability fields of Fe-brucite, greenalite, Fe-cronstedtite, and hisengirite in the Fe-Si-H₂O system are indicated by the green lines. Violet lines indicate phase boundaries involving Mg-cronstedtite (Mg-Fe-1715 1716 Si-H₂O system):

1717 (1) MgCtd-Brc-FeBrc: $2Mg_2Fe^{3+}Si Fe^{3+}O_5(OH)_4 + 4H_2O = 4Mg(OH)_2 + 4Fe(OH)_2 + 2SiO_2 + O_2$:

1718 (2) MgCtd-FeBru-Ctl: $6Mg_2 Fe^{3+}Si Fe^{3+}O_5(OH)_4 + 2SiO_2 + 8H_2O = 12Fe(OH)_2 + 4Mg_3Si_2O_5(OH)_4 + 3O_2;$

- 1719 (3) $MgCtd-Ctl-Gre: 6Mg_2 Fe^{3+}Si Fe^{3+}O_5(OH)_4 + 10SiO_2 + 4H_2O = 4Mg_3Si_2O_5(OH)_4 + 4Fe_3Si_2O_5(OH)_4 + 3O_2.$
- 1720 The stability of reaction (3) with respect to hisingerite was not calculated and hence this reaction is shown as a 1721 dashed violet line where hisingirite is stable in the Mg-free system. Temperature dependent fO_2 set by the 1722 intersections between lines (1) and (2) and lines (2) and (3) in the right panel are shown by the two violet curves 1723 in the left panel:
- 1724 (4) MgCtd-FeBrc-Ctl-Gre: $2Mg_2 Fe^{3+}Si Fe^{3+}O_5(OH)_4 + 3H_2O = 4Fe(OH)_2 + Mg(OH)_2 + Mg_3Si_2O_5(OH)_4 + O_2$
- 1725 (5) MgCtd-FeBrc-Brc-Ctl: 6Mg2 Fe³⁺Si Fe³⁺O5(OH)4 + Fe₃Si₂O5(OH)4 + 9H₂O=15Fe(OH)₂ + 4Mg₃Si₂O₅(OH)4 + 3O₂
- 1726 Temperature-dependent fO₂ set by the greenalite, Fe-cronstedtite, and Fe-brucite assemblage, which is at green
- 1727 triple point in the right panel, is equivalent to the green curve in the left panel:
- 1728 (6) Ctd-Gre-FeBrc: $2Fe^{2+}{}_{2}Fe^{3+}SiFe^{3+}O_{5}(OH)_{4} + 3H_{2}O = 5Fe(OH)_{2} + Fe_{3}Si_{2}O_{5}(OH)_{4} + O_{2}$
- 1729

Thus, to summarize, brucite - serpentine reactions [(± andradite, *J A M Leong et al.*, 2021b], can
potentially explain fO₂, pH and dissolved SiO₂ contents observed in reduced water at depths greater
than 250 meters in BA1A 2018, BA1D 2019, and BA4A 2018, together with the pH and dissolved SiO₂
contents in even more reduced waters observed in BA3A 2018, NSHQ14 2018, and BA2A 2018.
While minor phases clearly record fO₂, pH and/or aSiO₂ conditions in this range, we propose that
minerals composed of major elements in the rock largely control these conditions.

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1737 Finally, water in BA1A 2017, BA1B 2018, BA2A 2017, and probably BA1D 2018, apparently records 1738 addition of fresh, high fO_2 water during drilling, suggesting that more than six months may be required 1739 for water in these Holes to reach steady state variation in fO₂ vs depth. Water in BA3A 2018 – highly reduced from top to bottom, and very similar to water in nearby Hole NSHQ14 drilled more than ten 1740 years before logging - appears to be an exception to this "rule". In interpreting the logging data, an 1741 1742 additional factor to consider is that flow measurements indicated that (a) there is a relatively fast flowing, low pH aquifer near the top of BA1A, and 9b) water flowed down the upper part of BA1A for 1743 more than a year after drilling, possibly because this is the natural process, and possibly because the 1744 1745 borehole connected two previously isolated aquifers.

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5. Conclusions

In this paper, we've provided an overview of some initial results from the Oman Drilling Project's Multi-1749 Borehole Observatory (MBO). Investigations of water and rock samples, from three cored and four 1750 1751 rotary boreholes in the MBO have yielded a wealth of new information, which we have just begun to understand. Host rocks to the boreholes are partially to almost completely serpentinized residual 1752 harzburgites and replacive dunites from the upper few kilometers of the mantle section of the Samail 1753 ophiolite. Dunites show evidence for "reactive fractionation", in which cooling, crystallizing magmas in 1754 the uppermost mantle continued to react with surrounding harzburgites, producing a distinctive trend 1755 of incompatible element enrichment at high, nearly constant Ni concentrations and molar Mg#'s. 1756 1757 These mantle lithologies have been 65 to 100% hydrated, to form serpentine and other minerals. 1758 Similarly, the ferric to total iron ratio in core varies from 50 to 90%.

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1760 In the deepest cored hole, BA1B, the extent of hydration, oxidation, and carbonate vein formation all 1761 decrease systematically with increasing depth below the surface, and gradients in borehole water 1762 composition are correlated with variation in core composition, suggesting that much of the alteration is relatively young, ongoing, and related to low temperature weathering. This inference is borne out by 1763 the presence of young serpentine veins, which are intergrown with, and locally crosscut, carbonate 1764 veins with measurable ¹⁴C contents, yielding a mass fraction rate of "serpentinization" ~ 10⁻¹⁵/s. 1765 1766 Hydration is accompanied by ongoing SiO₂ addition to all but the most silica rich dunite and harzburgite compositions. We hypothesize that sulfur enrichment at 30 to 150 m depth, is related to 1767 ongoing, oxidative leaching of sulfur from the upper 30 m, together with sulfate reduction and sulfide 1768 precipitation in an underlying zone of supergene enrichment. 1769

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Borehole waters below 200 to 250 m depth, and some mineral assemblages in core, record oxygen 1771 1772 fugacity at and approaching the low fO₂ limit where H₂O forms H₂. In Holes BA2A and BA3A, plus 1773 older water monitoring well NSHQ14, fO_2 in water appears to be fixed by a combination of the H₂O to 1774 H₂ reaction itself, together with ongoing oxidation of remaining ferrous iron in serpentine, brucite and 1775 olivine. This is intriguing, because discrete sampling of water in the MBO has not yet produced compositions saturated in H₂ gas, and the origin of H₂ streaming from some peridotite-hosted alkaline 1776 springs elsewhere in the Samail ophiolite is debated. 1777

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1779 In water properties logged more than one year after drilling, in Holes BA1A and BA1D, and in logging data from Hole BA4A just a few months after drilling, fO₂ appears to approach an asymptotic value 3 1780 to 4 log units above the H_2O-H_2 buffer. We hypothesize that this is due to equilibria involving 1781 cronstedtite ((Mg, Fe²⁺)₂Fe³⁺SiFe³⁺O₅(OH)₄, chrysotile ((Mg, Fe²⁺)₃Si₂O₅(OH)₄), and brucite 1782 $(Mq, Fe^{2+})(OH)_2$, with cronstedtite compositions close to the Ma-endmember $Mq_2Fe^{3+}SiFe^{3+}O_5(OH)_4$ 1783 due to the high molar ratio of $Mg/(Mg+Fe^{2+})$ in the rocks, in turn related to extensive iron oxidation. 1784 1785 This mineral assemblage, ± the minor phase and radite which is commonly intergrown with serpentine 1786 in drill core, may control the limited range of pH (10-11.3) and dissolved SiO₂ observed in waters from the MBO below 200 to 250 meters depth, and in peridotite-hosted alkaline springs throughout the 1787 1788 Samail ophiolite.

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1790 Despite all of these indications of ongoing interaction between borehole water and surrounding rocks, including the inference that fluid-mineral equilibria may be controlling the present-day composition of 1791 1792 water in the peridotite-hosted aguifer at the MBO, there are many striking indicators of "diseguilibrium" in the core. Especially in Hole BA1B, where logging a few months after drilling revealed a gradient in 1793 the pH and fO₂ extending downward for 400 meters, borehole waters are more oxidized than 1794 1795 recorded by key minerals and mineral assemblages in core. On a much smaller spatial scale, Ellison 1796 et al. [2021] showed that the ferric to total iron ratios in serpentine was highly variable and correlated

with texture at the microscale. Similarly, as shown by de Obeso and Kelemen [2020], some peridotite
outcrops elsewhere in the Samail ophiolite preserve almost the entire range of fO₂ on Earth, over a
length scale ~ 10 cm, from native metals and highly reduced sulfides in dark serpentinites to rusty
orange, clay-bearing assemblages in which all iron is ferric. These different micro-environments
record very different oxidation states which could all be present in peridotite-hosted aquifers at the
same time, juxtaposed on short length scales.

It is likely that many of these variations are correlated with texture, in which reduced, low SiO₂ 1804 assemblages in mesh cores that record very low water/rock ratios are juxtaposed with adjacent veins 1805 1806 recording much higher ratios as reported in core from Hole BA3A by Ellison et al. [2021], and by other workers for outcrop samples and drill core worldwide [e.g., Bach et al., 2004; Bach et al., 2006; J.S. 1807 1808 Beard et al., 2009; Frost et al., 2013]. Of course, there are exceptions. Ellison et al. also reported that 1809 in samples from above 100 m depth in BA3A, mesh cores generally contained serpentine instead of 1810 brucite, and that the latest serpentine veins were more reduced. These observations likely reflect multiple levels of reaction progress (multiple water/rock ratios) and multiple controls on Fe oxidation 1811 1812 state in serpentine.

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1814 Despite the observed local variability described in the last two paragraphs, overall, on the basis of 1815 observed gradients in bulk rock alteration with depth, we infer that the proportion of reduced mesh 1816 cores vs relatively oxidized veins increases with depth, and that the difference in fO₂ recorded in 1817 cores and veins decreases with depth. Moreover, we suggest that most of the diverse mineral 1818 assemblages observed in core could have formed concurrently, at a close approach to equilibrium, on 1819 time scales ~ 10,000 years, and indeed that most of these assemblages are continuing to form today. 1820

In general, we hope this paper will be viewed as a starting point, for discussion, and more importantly
for continued investigation. Most of the core is intact, and most of the boreholes remain open, for
continuing research.

6. Author contributions

1827 Peter Kelemen wrote most of the manuscript, asked James Leong and others a lot of questions, and 1828 developed some ideas on the genesis and evolution of peridotite protoliths, changes in bulk rock 1829 composition due to alteration, and – with Leong – fluid-mineral controls on fO₂, aSiO₂, pH and other 1830 parameters. Leong led the team in thermodynamic calculations and modeling, and tried to educate Kelemen, while Juan Carlos de Obeso conducted microprobe analyses of serpentine and minor 1831 phases including chlorite, and radite and grossular, and performed X-Ray diffraction, carbon, oxygen 1832 1833 and strontium isotope analyses of carbonate vein samples. Jürg Matter led the borehole logging effort, and has generously provided the entire OmanDP Science Team with access to the resulting 1834 data. Eric Ellison, assisted by Dan Nothaft, provided valuable input on calculation of fO₂ from Eh, pH, 1835 temperature and pressure data for observed borehole waters, and fO₂ for the corresponding limit 1836 where H_2O is reduced to form H_2 at a given temperature and pressure, together with the uncertainty in 1837 these values. Alexis Templeton, together with Ellison, shared preprints and ideas, in essential 1838 1839 discussions that helped frame the questions asked, and the tentative answers provided, in this paper. 1840 Compositions of borehole and spring water samples were compiled by Leong et al. (2021), but of course we are greatly indebted to all those who actually gathered and analyzed those samples, via 1841 borehole sampling led by Templeton, Nothaft and Ellison, among others. As always, Marguerite 1842 1843 Godard ensured the high quality of geochemical data collected onboard DV Chikyu. Matter was ably 1844 assisted in downhole logging of Eh, pH, temperature, pressure and depth in borehole waters by 1845 Philippe Pézard and his research team. Jude Coggon and Nehal Warsi supervised 100% of core recovery operations. Coggon was also essential as Project Manager throughout the duration of 1846 OmanDP and beyond, recalibrating the XRF data and editing the Proceedings chapters long after the 1847 money was gone. Coggon and Saebyul Choe were staff scientists, while Godard, Kelemen, Katsu 1848 1849 Michibayashi, Eiichi Takazawa and Damon Teagle were co-Chief Scientists onboard DV Chikyu during the monthlong description of 1 km of core from Holes BA1B. BA3A and BA4A. Kelemen. 1850 Matter and Teagle were co-PI's of the ICDP Oman Drilling Project, and Zaher Sulaimani was In-1851 1852 Country Project Manager.

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1902 Data availability: The data in this paper will be uploaded to the EarthChem and/or Pangaea
 1903 repositories upon acceptance of this paper.
 1904

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Supplementary Information



Supplementary Section 1: Results of thermodynamic calculations f or equilibria involving Oman fluids, serpentine and brucite.

Methods used for these calculations, and general results, are described in the main text, Section 2.5.

Supplementary Figure S1: Extent of disequilibrium (in kilojoules per reaction) for the brucite (top panel) and chrysotile (bottom panel) dissolution reactions in various peridotite-hosted Samail ophiolite fluid compositions reported in previous studies. Horizontal green line depicts fluid with pH ranging from 11 to 12, at 40 °C, the pressure of sampling (1 bar for surface samples) and fO2 at the H₂O-H₂ stability limit, in equilibrium with chrysotile and brucite. Surface fluids in grey squares: Paukert et al. ([Paukert et al., 2012]), Canovas et al. ([Canovas et al., 2017]), Leong et al. ([Leong et al., 2021]). Borehole fluids in black symbols: diamonds, Rempfert et al. ([Rempfert et al., 2017]); squares, Paukert Vankeuren et al. ([Paukert Vankeuren et al., 2019]); triangles, Nothaft et al. ([Nothaft et al., 2021a; Nothaft et al., 2021b]). Positive ΔG indicates that the fluid is saturated in brucite or chrysotile; negative values indicate that the fluid is undersaturated in brucite or chrysotile.





Supplementary Figure S2: Extent





Supplementary Section 2: Concentration of dissolved H₂ in borehole water samples compared to the sum of concentrations of other redox-sensitive solutes



Supplementary Figure S4: Concentration of dissolved H_2 vs the sum of concentrations of all other redox sensitive, dissolved species (CH4, HS-, NH4+, Fe+2) measured in discrete samples recovered from >50 m depth in MBO boreholes. Yellow, green, blue, and black symbols correspond to samples from BA1A, BA1D, NSHQ14 (nearby BA3A), and NSHQ04, respectively. Triangle, diamond, and square symbol represent data from Nothaft et al. [2021a; 2021b], Rempfert et al. [2017], and Paukert Vankeuren and co-workers [Paukert et al., 2012; Paukert Vankeuren et al., 2019], respectively.

Supplementary Section 3: Propagation of uncertainty for estimates of fO₂ based on measurements of Eh, pH and temperature

Methods for calculating fO_2 from measurements of Eh, pH and temperature are described in Section 2.6, with results described in the text and illustrated in Figures 24, 28 and 30, as well as Supplementary Figure S3. We developed formalism for propagation of uncertainty for these calculated fO_2 values, which is presented here.

The formal uncertainty of log(fO₂) and log(fO₂(limit) in equations 5 and 6 in the main text can be calculated by assuming that the uncertainty in the measured E_h (σ_{Eh}) was 10 mV, the uncertainty in pH (σ_{PH}) was 0.1, the uncertainty in temperature (σ_T) was 0.05 K, and the uncertainty in pressure (σ_P) was 5 bars. These were determined by multiplying the manufacturer specifications for uncertainty of the instruments **by a factor of 10** for a conservative estimate of the real uncertainty in the field. These errors were propagated through the calculations above by taking the partial derivative with respect to Eh, pH, T, and P, multiplying by the corresponding uncertainty, and adding in quadrature, i.e.:

$$\sigma_{\log (fO_2)} = \sqrt{\left(\frac{\partial \log (fO_2)}{\partial E_h}\right)^2 \sigma_{Eh}^2 + \left(\frac{\partial \log (fO_2)}{\partial T}\right)^2 \sigma_T^2 + \left(\frac{\partial \log (fO_2)}{\partial pH}\right)^2 \sigma_{PH}^2}$$
$$\sigma_{\log (fO_{2(limit)})} = \sqrt{\left(\frac{\partial \log (fO_{2-limit})}{\partial T}\right)^2 \sigma_T^2 + \left(\frac{\partial \log (fO_{2(limit)})}{\partial P}\right)^2 \sigma_P^2}$$

Which reduces to:

$$\sigma_{\log (fo_2)} = \sqrt{\left(\frac{20159.1}{T}\right)^2 \sigma_{Eh}^2 + \left(\frac{19174 - 20159.1E_{measured}}{T^2}\right)^2 \sigma_T^2 + 16\sigma_{pH}^2}$$

$$\sigma_{\log(fO_{2(limit)})} = \sqrt{\left(\frac{29433.8}{T^2}\right)^2 \sigma_T^2 + \left(\frac{-2}{\ln(10)P}\right)^2 \sigma_P^2}$$

Finally, the uncertainty in $\Delta \log(f02) = \log(f0_2) - \log(f0_{2(\text{limit})})$ is:

$$\sigma_{\Delta \log(fO_2)} = \sqrt{\sigma_{\log(fO_2)}^2 + \sigma_{\log(fO_2(limit))}^2}$$

Again, we assumed that actual measurement errors in field conditions were **about** ten times larger than the formal uncertainties arising from formal propagation of the manufacturer-provided uncertainties in measurements. As a result, hese calculations yield estimates of uncertainty that are $\leq \pm 1 \log$ unit of (fO₂) in bars. Also, as noted in Section 2.6, the fO₂ values calculated from Eh, pH and temperature measurements should be regarded as approximate because the fluids may contain multiple, redox sensitive solutes that are not in mutual equilibrium. Thus, there are several qualitative elements contributing to the actual uncertainty of the fO₂ estimates. As a result, we have not tabulated or illustrated the specific uncertainties for each fO₂ value. Instead, we infer and illustrate uncertainty bounds of $\pm 1 \log$ unit of fO2 in Figure 30.



Supplementary Section 4: Sulfur concentration vs depth in Hole BA4A

Figure S5: Sulfur concentration versus depth in core from Hole BA4A [Kelemen et al., 2021]. Sulfur concentrations below the detection limit of shipboard analyses were assigned a value of 0.01 wt% (100 ppm). Orange bar illustrates previously measured range of sulfur concentration in mantle harzburgites and dunites in the Samail ophiolite, from 5 to 500 ppm [Hanghøj et al., 2010; Oeser et al., 2012]. Dunites: light green circles; harzburgites: dark green squares.

Supplementary Section 5: Evaluation of the hypothesis that addition of igneous minerals to residual mantle harzburgites produced low Mg/Si at a given Al/Si in core samples from the MBO

As shown in Figure 26 and discussed in Section 4.3 in the main body of the paper, core samples of harzburgite from Holes BA1B, BA3A and BA4A have low wt% MgO/SiO₂ at a given wt% Al₂O₃/SiO₂ (hereafter, Mg/Si and Al/Si for brevity) compared to the residues of partial melting and melt extraction from the mantle. The discussion in the main text mentions three possible reasons for low Mg/Si at a given Al/Si in these samples: (1) Mg dissolution and removal from the rocks (2) Si addition, and (3) igneous "impregnation", for example by crystallization of small amounts of relatively Al-rich, Si-rich, Mg-free plagioclase feldspar in pore space in residual peridotites in the shallow mantle. This section of the Supplementary Information evaluates, and rejects, the third of these hypotheses. We do this primarily graphically, with a minimum of explanatory text.

The terms "impregnated peridotite", "impregnated dunite", and sometimes (usually, erroneously) "troctolite" are used to refer to rock with added, igneous minerals precipitated during migration of melt through pre-existing, residual mantle peridotites and dunite conduits, as outlined in Sections 1.2 and 4.1 of the main text. 100% crystallization of added melt would produce a geochemical trend more or less identical to the melt extraction trend illustrated by the red symbols in Figure 26. However, commonly the minerals added to impregnated peridotites are "cumulate", in the sense that they are precipitated by partial crystallization of a melt, after which the remaining melt is removed from the rock. In various cases, the presence of individual minerals (typically, calcium-rich pyroxene, cpx, and/or plagioclase, but in some cases Ca-poor pyroxene, opx), or mixtures of these minerals, are attributed to impregnation.



Figure S6: For reference the residues of melt extraction from Figure 26 are plotted again here.

As an end-member residual peridotite, we use a harzburgite with 10 wt% opx, 90 wt% olivine, a molar Mg# (molar Mg/(Mg+Fe)) of 0.9, and Al/Si of 0.005 (perhaps with Al in spinel), ~ 42.6 wt% SiO₂, 0.2 wt% Al₂O₃, 9.0 wt% FeO and 48.2 wt% MgO.

The mineral plagioclase is a solid solution primarily composed of end-members anorthite (CaAl₂Si₂O₈) and albite (NaAlSi₃O₈). Neither addition of 4 wt% anorthite, nor addition of 4 wt% albite, reproduces the compositions of MBO harzburgites illustrated in Figure 26.



Figure S8

There are many sources of data on mineral compositions in peridotites from the Samail ophiolite. For brevity and simplicity, here we simply use averages from the extensive data of Monnier et al. [2006]. Neither 10 wt% addition of cpx, nor 10 wt% addition of opx, reproduces the compositions of MBO harzburgites illustrated in Figure 26. Addition of more than 10 wt% either pyroxene would produce CaO and/or SiO2 concentrations much higher than in most MBO harzburgites, and optically evident, high pyroxene abundances that are not observed in MBO core.



Figure S10

We also tested various mixtures of minerals, which also failed to reproduce the compositions of MBO harzburgites illustrated in Figure 26.





As a result of these and several other, related calculations, we conclude that igneous impregnation cannot explain the low Mg/Si at a given Al/Si observed in MBO harzburgites (Figure 26).

Supplementary Section 6: Plots of Mg/Si deficit vs Mg# and depth

As noted in Section 4.3 of the main text, if the observed low Mg/Si in MBO harzburgites were due to Mg extraction, one would expect to see a correlation between the Mg/Si deficit (equation 9) and Mg# (molar Mg/(Mg+Fe)). In Figure S12, we show that such correlations are not observed, and futher that there is no correlation between the Mg/Si defict with depth in the cored MBO Holes.







Figure S14: Plots of Mg/Si deficit vs Mg# and depth for the three cored MBO Holes.
Supplementary Section 6: Additional results of reaction-path modeling

Figure 29 in the main text presents results of reaction path modeling at 35°C and 50 MPa. The righthand panels in that figure illustrate results from Step 2 of the modeling, involving reaction of Type 1, Mg-HCO3 rich waters with peridotite, isolated from the atmosphere, as described in Sections 2.5 and 4.6. Here, in Figure S13, we provide a few more results from Step 2. We invite readers to look at the caption for Figure 29 to aid in understanding Figure S13.



Figure S13: Additional results from reaction path modeling at 35°C and 50 MPa, as described in Sections 2.5 and 4.6, and presented in Figure 29. Here we provide some details of phase proportions and compositions, as well as the calculated partial pressure of dissolved H₂ produced in the model. In addition to results described in the text and the caption for Figure 29, the main point to take from this figure is information about the composition of precipitating brucite and serpentine solid solutions. Initially, at water/rock ratios greater than 100, precipitating serpentine is composed almost entirely of (Mg,Fe²⁺)₂Fe³⁺SiFe³⁺O₅(OH)₂ - Mg-Fe²⁺-cronstedtite, with molar Mg/(Mg+Fe²⁺), or Mg#, close to 1. With increasing reaction progress, at water/rock ratios less than 100, brucite begins to crystallize, with increasingly large proportions of Fe²⁺ (lower Mg#) and no Fe³⁺, while the serpentine solid solution contains increasingly large amounts of greenalite and chrysotile components. Both of these factors lead to increasingly low Fe³⁺/(Fe total) in the crystallizing phase assemblage. Thus, Fe³⁺/(total Fe) in the serpentine solid solution drops by a factor of about 5, and Fe³⁺/(total Fe) in the total crystallizing assemblage drops by a factor of ~ 10. However, meanwhile, the mass of crystallized serpentine + brucite increases by more than a factor of 100 during reaction progress from water/rock ratio of ~ 100 to 10^{-0.8}. As a result, as shown in Figure 29, the total amount of Fe²⁺ that is oxidized to form Fe³⁺ continues to increase throughout the reaction path, together with decreasing fO₂ and an increasing partial pressure of H₂.

To reiterate, (déjà vu all over again!) the reaction path modeling was done at a pressure 50 MPa, whereas the maximum pressure at the bottom of MBO boreholes is ~ 4 MPa. At 4 MPa and 35°C, the partial pressure of H₂ would not increase above 4 MPa, fO₂ would be limited to a maximum value of ~ 10⁻⁸³, but oxidation of Fe²⁺ to Fe³⁺ would proceed, together with formation of H₂ gas.

Supplementary Section 7: References cited in this supplement

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COLUMBIA UNIVERSITY IN THE CITY OF NEW YORK DEPARTMENT OF EARTH & ENVIRONMENTAL SCIENCES LAMONT DOHERTY EARTH OBSERVATORY

June 30, 2021

Dr. Isabelle Manighetti Editor in Chief, JGR Solid Earth

Dear Dr. Manighetti,

As required, I am including this letter with my submission of a multi-authored paper, "Ongoing alteration of mantle peridotite in the weathering horizon: Initial results from the Oman Drilling Project Multi-Borehole Observatory", explaining how its completion was delayed by the impacts of the COVID-19 disease.

If this paper is accepted, I am requesting that it be included in the Special Issue on Ophiolites and Oceanic Lithosphere. My understanding is that the paper will go through the JGR peer-review process, that it will be accepted or declined on the basis of that normal process, and – if accepted – that it will be incorporated into the Special Issue.

This paper has been delayed by the impacts of the COVID-19 disease in the following direct and indirect ways.

First and foremost, this is an overview of scientific results related to Oman Drilling Project Holes BA1A, BA1B, BA1C, BA1D, BA2A, BA3A and BA4A. As such, completing this paper required completion of analytical work by many investigators around the world. In turn, this work was delayed by the disease. As it is, the manuscript I am submitting contains references to several substantial papers that are still in preparation or in revision.

Just among the examples that I personally know about in detail, these delays were due in part to

(1) the fact that I became very ill – perhaps from COVID-19 – upon my return from Oman in late January 2020 (it turned out that at least one attendee of our conference there had the disease),

(2) postdoc Juan Carlos de Obeso contracted the disease and was unable to work for a few weeks,

(3) postdoc Juan Carlos de Obeso was unable to access closed laboratory facilities at Lamont Doherty Earth Observatory for several months,

(4) postdoc Juan Carlos de Obeso's mother-in-law, who is ill with cancer, needed his and his wife's help to move from France to Mexico during the pandemic, and then to convalesce in Mexico, and when Juan Carlos went to Mexico he became subject to various mandatory quarantine and travel restrictions,

(5) as a result of factors 2 through 4, Dr. de Obeso was unable to complete his planned analyses of ⁸⁷Sr/86Sr and d¹³C, and their interpretation, crucial to this paper, and his companion paper, until November (he is still revising a related paper for submission),

(6) our older daughter and her partner had to abandon plans and live with us while not working for several months,

(7) our younger daughter had to leave Colorado College and live with us while completing her final year of coursework online,

(8) in the midst of 6 & 7, we had to unexpectedly extend our rental of a house in Boulder Colorado, and then move twice, first from Boulder to our rental property in Woods Hole (which fortunately was not occupied at the time), and then from Woods Hole to our house in New York (to make room for tenants in Woods Hole),

(9) as a result of 1-8, I did not complete a submittable draft of this paper before starting teaching in the fall semester, after which almost all my time through the end of December was occupied by teaching because

(9a) an unprecedented number of students enrolled in my courses on "Earth Resources & Sustainable Development" (an unprecedented total of 145 completed the courses), requiring that I double my time commitment for recitation sections, and

(9b) I had to set up a new home office and learn how to teach online because my course was 100% remote,

(10) and in addition to teaching, the delay in completing this paper caused its completion to compete for my time with other significant commitments I had made, which could not be postponed, including (10a) participation in the Mars 2020 Rover Science Team, and

(10b) advising two startup companies and several larger companies on CO2 removal from air and permanent storage via carbon mineralization.

(11) From May 2020 through March 2021, we made unprecedentedly frequent, distanced visits to my wife's parents (divorced, two different homes) based on her concern about them, and

(12) we had to make special arrangements to accommodate our daughter over the winter holidays because she contracted COVID-19 en route from Colorado to New York.

Meanwhile, new postdoc James Leong was delayed

(13) in completing his dissertation, then

(14) delayed in renewing his visa (he is Filipino), and then

(15) delayed in starting his postdoc at Lamont (Columbia had

(15a) a hiring freeze, and once that was waived he still had to

(15b) complete a month-long quarantine period, and then

(15c) receive an up-to-date, negative COVID-19 test in order to satisfy the requirements our labs, which took more than a week at that time.

In turn, Dr. Leong's modeling expertise was central to completing calculations essential for this paper.

This is the second of two papers I have submitted to JGR this spring, for incorporation into the Special Issue on Ophiolites and Oceanic Lithosphere. I wrote them in order, and thus did not complete this one until the other was complete and submitted. Research essential to the other paper was even more seriously delayed by the effects of the COVID-19 pandemic.

Those are the reasons for the delays whose details I know about personally.

Finishing this paper also required completion of geochemical analyses by Marguerite Godard at the University of Montpellier (paper in prep for JGR), completion of work by Eric Ellison, Alexis Templeton, Dan Nothalf and others on analyses of rock cores and water samples, and so on. I am sure that most or all of these other scientists could supply a similarly long list of reasons for delay of their work, related directly or indirectly to the pandemic.

I hope that you find this letter informative.

Sincerely,

Pa B Kn

Peter B. Kelemen Arthur D. Storke Professor Dept. of Earth & Environmental Sciences peterk@LDEO.columbia.edu

cc: Steve Parman, Editor, JGR Solid Earth