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1 **Listvenite formation during mass transfer**
2 **into the leading edge of the mantle wedge:**
3 **Initial results from Oman Drilling Project Hole BT1B**
4

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21

22 **Abstract**

23 This paper provides an overview of research on core from Oman Drilling Project Hole BT1B and the
24 surrounding area, plus new data and calculations, constraining processes in the Tethyan subduction
25 zone beneath the Samail ophiolite. The area is underlain by gently dipping, broadly folded layers of
26 allochthonous Hawasina pelagic sediments, the metamorphic sole of the Samail ophiolite, and
27 Banded Unit peridotites at the base of the Samail mantle section. Despite reactivation of some faults
28 during uplift of the Jebel Akdar and Saih Hatat domes, the area preserves the tectonic “stratigraphy”
29 of the Cretaceous subduction zone. Gently dipping listvenite bands, parallel to peridotite banding and
30 to contacts between the peridotite and the metamorphic sole, replace peridotite at and near the basal
31 thrust. Listvenites formed at less than 200°C and (poorly constrained) depths of 25 to 40 km by
32 reaction with CO₂-rich, aqueous fluids migrating from greater depths, derived from devolatilization of
33 subducting sediments analogous to clastic sediments in the Hawasina Formation, at 400-500°. Such
34 processes could form important reservoirs for subducted CO₂. Listvenite formation was accompanied
35 by ductile deformation of serpentinites and listvenites – perhaps facilitated by fluid-rock reaction – in a
36 process that could lead to aseismic subduction in some regions. Addition of H₂O and CO₂ to the
37 mantle wedge, forming serpentinites and listvenites, caused large increases in the solid mass and
38 volume of the rocks. This may have been accommodated by fractures formed as a result of volume
39 changes, mainly at a serpentinization front.
40

41 **Plain language summary**

42 This paper reports initial results from study of core from Oman Drilling Project Hole BT1B and the
43 surrounding area. It provides insights into subduction zone processes, including large fluxes of
44 recycled CO₂ from subducting sediments into the leading edge of the mantle wedge, and surprisingly
45 low temperature ductile deformation at less than 200°C. Recycling of CO₂ via carbon mineralization in
46 the hanging wall of subduction zones may produce an important, lithospheric reservoir in the global
47 carbon cycle. Ductile deformation of serpentinite, and during or after transformation of peridotite to
48 listvenites (mixtures of carbonates and opal or quartz) could explain aseismic subduction atop some
49 subduction zones.

1. Introduction

Oman Drilling Project (OmanDP) Hole BT1B at 23.364374°N, 58.182693°E, about 12 km southeast of the town of Fanjah in the Sultanate of Oman, sampled serpentinitized peridotites and listvenites (fully carbonated peridotites, Halls & Zhao 1995) at the base of the Samail ophiolite, the basal fault of the ophiolite, and the underlying metamorphic sole, with the intention of investigating mass transfer and deformation in the “leading edge of the mantle wedge” overlying a Tethyan subduction zone. Study of outcrops along the contact between the sole and the peridotite can illuminate processes in and above a subduction zone that are generally inaccessible to direct observation. Of particular interest are (a) the source of footwall fluids, (b) the nature and mechanism of fluid transport along the thrust fault and into the mantle wedge, (c) chemical, mineralogical and rheological modification of the hanging wall by reaction with footwall fluids, and (d) the mechanisms of subduction zone deformation.

Hole BT1B was drilled using cylindrical diamond bits and wireline core retrieval, from March 7 to March 23, 2017. Core recovery was ~ 100% throughout the Hole. Core was 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 Drilling Program (currently, the International Ocean Discovery Program, IODP). Detailed core descriptions, together with drilling history and some background information (Kelemen et al 2020b, Kelemen et al 2020c) are available online at http://publications.iodp.org/other/Oman/VOLUME/CHAPTERS/113_BT1.PDF

This paper reports new mapping and structural observations, mineral analyses and modeling, together with a summary of prior observations. It is intended to provide interpretive context for more detailed studies of core from Hole BT1B and the geology of the surrounding region. Such studies in this Special Issue of the Journal of Geophysical Research include those focused on textural and petrologic data for listvenites (Beinlich et al 2020) and the metamorphic sole (Kotowski et al 2021), volume changes during serpentinitization (Malvoisin et al 2020), major and trace element geochemistry with relevance to subduction zone mass transfer (Godard et al 2021, Okazaki et al 2021), Mg-, Sr- and C-isotope geochemistry constraining the source of CO₂-bearing fluids and the fluid-rock reaction process (de Obeso et al 2021a, de Obeso et al 2021b) and deformation of the listvenites (Menzel et al 2020, Menzel et al 2021).

Section 2 provides geological context for observations of core and surrounding outcrops. Section 3 summarizes methods used to produce results presented for the first time in this paper. Section 4 reports new geological field observations and analytical data, and reviews key results from Kelemen et al. (2020b) in context. Section 5 discusses the pressure, temperature and timing of listvenite formation, the nature and source of the fluids that transformed mantle peridotite into serpentinite and listvenite, the chemical and mechanical processes during these transformations, and deformation of altered mantle peridotite immediately above a paleo-subduction zone beneath the “leading edge of the mantle wedge”.

90

91 It is hoped that this paper, and the other papers in this Special Issue, will provide a starting point for
92 future investigations of this unique and important site. In this context, readers should be aware that
93 the archive half of the core is currently stored at Petroleum Development Oman where it is available
94 for viewing, the working half of the core is stored at the American Museum of Natural History, where it
95 can be sampled upon request to the Museum, and a huge volume of data from shipboard visual core
96 observations and analytical data is available to anyone at
97 <http://publications.iodp.org/other/Oman/OmanDP.html> , [https://www.icdp-](https://www.icdp-online.org/projects/world/asia/oman/)
98 [online.org/projects/world/asia/oman/](https://www.icdp-online.org/projects/world/asia/oman/), and other sites that can be accessed from there.

99

100

2. Geological setting

101

102

2.1 Regional geologic context

103

104 The Samail ophiolite is composed of oceanic crust formed at a submarine spreading center above a
105 subduction zone. The crustal thickness and composition of the ophiolite is similar to the geophysically
106 and geologically constrained characteristics of fast-spreading, Pacific oceanic crust, with a few km of
107 submarine lavas and sheeted dikes overlying a thicker, gabbroic lower crust (e.g., Christensen &
108 Smewing 1981, Coleman & Hopson 1981, Nicolas et al 1996) However, the lavas have a trace
109 element “subduction signature” (Alabaster et al 1982, Pearce et al 1981, Pearce & Peate 1995), and
110 parental, mantle-derived magmas appear to have contained 0.2 to 2 wt% H₂O, substantially more
111 than in primitive mid-ocean ridge basalts (MacLeod et al 2013). Beneath the crustal section of the
112 ophiolite, residual mantle peridotites and tabular dunites record polybaric decompression melting,
113 melt extraction, and focused transport of basaltic melt upward to form the crust (Braun & Kelemen
114 2002, Godard et al 2000, Kelemen et al 2000, Kelemen et al 1995, Monnier et al 2006).

115

116

2.2 Lithologies at the base of the Samail ophiolite

117

118 Here we describe the units above and below the basal fault of the Samail ophiolite. We begin with a
119 review of work on the metamorphic sole. Then, we describe the overlying Banded Unit at the base of
120 the ophiolite’s mantle section. Finally, we briefly outline the nature of the sedimentary rocks beneath
121 the metamorphic sole.

122

123 Beneath the mantle section of the ophiolite, and above allocthonous sediments of the Hawasina
124 Formation, are discontinuously exposed lenses of a “metamorphic sole”. Peak pressures and
125 temperatures in the sole generally record hot subduction conditions at temperatures up to 700-900°C
126 (Cowan et al 2014, Ghent & Stout 1981, Hacker & Gnos 1997, Searle & Cox 1999, Searle & Cox
127 2002, Searle et al 1980, Searle & Malpas 1980, Searle & Malpas 1982, Soret et al 2017) though at
128 BT1B peak temperatures are 450-550°C (Kotowski et al 2021). Apparently – based on published data
129 and calculations – the sole records a broad range of peak pressures from a possible lower limit of 200

130 MPa (Ghent & Stout 1981) or 800 MPa (Soret et al 2017) to a possible upper limit of 1400 MPa
131 (Cowan et al 2014, Searle & Cox 2002). Kotowski et al. (2021) report that the sole in core from Hole
132 BT1B records a peak pressure in the range of 800 to 1200 MPa.

133

134 The sole contains metasediments and meta-volcanic rocks – including submarine pillow lavas – with
135 the major element compositions of mid-ocean ridge basalts (MORB) as well as alkali basalts and
136 more evolved andesites and dacites (Alabaster et al 1982, Ernewein et al 1988, MacLeod et al 2013,
137 Pearce et al 1981, Searle et al 1980). In core from BT1B, alkaline metabasalt compositions in the sole
138 (Godard et al 2021, Kelemen et al 2020c) are unlike the magmas that formed the crust of the Samail
139 ophiolite. In the ophiolite, the structurally lowest, “Geotimes” or “V1” lavas are similar to normal mid-
140 ocean ridge basalts, though they probably were hydrous and they contain a hint of an arc trace
141 element signature (Alabaster et al 1982, Ernewein et al 1988, MacLeod et al 2013, Pearce et al
142 1981). Their composition, and that of dunite conduits for transport of primitive melts parental to V1
143 through the shallow mantle, is consistent with formation of the gabbroic lower crust in the Samail and
144 Wadi Tayin massifs of the ophiolite from primitive V1 magmas (Braun & Kelemen 2002, Kelemen et al
145 1997, Kelemen et al 1995). The overlying “Lasail” or “V2” lavas in the ophiolite are incompatible-
146 element-depleted, with a stronger subduction signature (Alabaster et al 1982, Ernewein et al 1988,
147 MacLeod et al 2013, Pearce et al 1981) and include boninites (e.g., Ishikawa et al 2002) as well as
148 tholeiitic basalts, andesites and dacites. Neither V1 nor V2 lavas are similar to the alkali basalt
149 compositions in the sole. The present day $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the alkali basalts in core from BT1B range
150 from 0.704 to 0.706 (de Obeso et al 2021a), more radiogenic than MORB. Though their Sr isotope
151 ratio may have been modified by alteration, one possibility is that the alkali basalts are remnants of
152 subducted seamounts with elevated $^{87}\text{Sr}/^{86}\text{Sr}$, similar to accreted seamounts along the Cascadia
153 margin of North America (e.g., Duncan 1982).

154

155 In addition to metabasalts, regionally the sole contains metasediments, and “exotic limestones”, all
156 incorporated by Searle and Malpas (1980) in the “Haybi Formation”. However, in this paper we
157 informally group the Haybi Formation into an undifferentiated metamorphic sole unit. In the sole
158 sampled by drill core from Hole BT1B, metasediments are clearly distinguishable from the
159 metabasalts based on texture, but some of them are compositionally similar to the metabasalts,
160 perhaps reflecting a volcanoclastic origin, whereas others grade into somewhat odd, low-SiO₂,
161 muscovite-bearing lithologies (Godard et al 2021, Kelemen et al 2020b, Kotowski et al 2021).

162

163 Above the sole – where it is present – and elsewhere at the base of the ophiolite, the lower few km of
164 the mantle section contains easily visible, meter to 10-meter scale, parallel bands of dunite,
165 harzburgite and (rare) lherzolite, informally known as the Banded Unit (Godard et al 2000, Khedr et al
166 2013, Khedr et al 2014, Linckens et al 2011, Lippard et al 1986, Prigent et al 2018a, Prigent et al
167 2018b, Takazawa et al 2003, Yoshikawa et al 2015). The lithological contacts in this unit are sharp.
168 They have low angle dips with respect to the paleo-seafloor, the crust-mantle transition zone, and the
169 basal fault that juxtaposes mantle peridotite with the metamorphic sole. Mylonitic shear zones are

170 present in the Banded Unit , with textures recording deformation at 700–1,000°C (Boudier et al 1988,
171 Herwegh et al 2016, Linckens et al 2011, Prigent et al 2018a). Thus, there is evidence for high strain
172 ductile deformation and transposition of layering at the base of the mantle section, which might have
173 accommodated substantial thinning (Prigent et al 2018a, Soret et al 2017). Similarly, there is evidence
174 for thinning of the units below the ophiolite (Grobe et al 2018, Grobe et al 2019).

175

176 While some of the range in temperature and pressure estimates from the sole and the Banded Unit
177 may be due to analytical and methodological uncertainty, or incomplete preservation and sampling of
178 the highest-grade rocks, some may be due to temporal and spatial variability in peak metamorphic
179 conditions. Moreover, the temperature record may be biased toward peak conditions, rather than later
180 cooling. At the initiation of subduction near a spreading ridge, hot metamorphic rocks from the footwall
181 may be accreted to the hot base of the newly formed mantle wedge, whereas as subduction zones
182 grow colder and develop a steady-state thermal structure, cold dense lithologies in the footwall may
183 be subducted (Agard et al 2016, Soret et al 2017). If so, the metamorphic sole in Oman may record
184 the anomalously high temperatures of subduction initiation, and not the lower temperatures of
185 evolution toward a steady-state subduction zone geotherm. The relatively low temperatures recorded
186 by the sole in BT1B core could represent a point along this cooling path (Kotowski et al 2021).

187

188 A close correspondence between 96 to 95 Ma igneous ages in the crust, and both $^{40}\text{Ar}/^{39}\text{Ar}$ and zircon
189 U/Pb ages of metamorphic rocks along the basal thrust (ca. 96-94 Ma), indicates that thrusting of the
190 Samail ophiolite over adjacent oceanic crust and nearby pelagic sedimentary units began during
191 formation of igneous crust in the ophiolite (e.g. , Garber et al 2020, Hacker & Gnos 1997, Hacker &
192 Mosenfelder 1996, Hacker et al 1996, Rioux et al 2012, Rioux et al 2013, Rioux et al 2016, Rioux et al
193 2021b, Stanger 1985, Styles et al 2006, Tilton et al 1981, Warren et al 2005) or perhaps even earlier
194 (Guilmette et al 2018).

195

196 The base of the metamorphic sole is truncated by a fault contact with autochthonous, low-grade
197 metasediments of the Hawasina Formation, composed of pelagic clastic units interlayered with
198 limestones (Béchenec et al 1990, Béchenec et al 1988). Relatively high, age corrected $^{87}\text{Sr}/^{86}\text{Sr}$
199 ratios in the clastic units suggest that they are distal sediments derived from erosion of continental
200 crust (de Obeso et al 2021a, Weyhenmeyer 2000), while carbonate units record Sr isotope ratios
201 similar to those of Mesozoic seawater (Weyhenmeyer 2000, Wohlwend et al 2017). These
202 sedimentary units were thrust over Mesozoic to Proterozoic rocks of the Arabian continental margin,
203 forming a “rumpled rug” between the autochthon and the ophiolite throughout northern Oman and the
204 eastern United Arab Emirates.

205

206 *2.4 History of the basal thrust of the Samail ophiolite*

207

208 Where the metamorphic sole is preserved, its tectonic contact with the mantle section of the ophiolite
209 represents a paleo-subduction zone at the base of the ophiolite, which consumed several hundred

210 kilometers of Tethyan basin and then continental crust before coming to rest on the Arabian
211 continental margin (Béchenec et al 1990, Béchenec et al 1988, Breton et al 2004, Cooper 1988,
212 Ninkabou et al 2021, Searle & Robertson 1990, van Hinsbergen et al 2019). During this time, the
213 overlying peridotite was “the leading edge of the mantle wedge”.

214

215 During coeval metamorphism of the sole and igneous accretion of the crust in the ophiolite, the
216 relative locations of these two units are uncertain. Primitive V1 magmas in the ophiolite, with
217 compositions almost indistinguishable from mid-ocean ridge basalts (MORB), crystallized to form
218 most of the crust, particularly in the southern Wadi Tayin and Samail massifs that were the site of of
219 the OmanDP boreholes. Like MORB worldwide, these magmas probably formed via polybaric
220 decompression melting over a depth interval of 75 km or more (e.g., Allegre et al 1973, Asimow et al
221 2004, Bottinga & Allegre 1973, Klein & Langmuir 1987, McKenzie & Bickle 1988). Thus, the
222 metamorphic sole (recording peak depths less than 40 km) must not have been directly beneath the
223 spreading center during crustal formation and metamorphism. Instead, the ophiolite section and the
224 metamorphic sole were juxtaposed after crust formation and after peak metamorphism in the sole.

225

226 Moreover, the structural thickness of the Samail ophiolite measured perpendicular to the paleo-
227 seafloor and/or the crust/mantle transition zone, and including both crust and mantle sections, never
228 exceeds ~ 20 to 30 km (Boudier & Coleman 1981, Nicolas et al 2000), corresponding to a pressure
229 less than or equal to ~ 800 MPa, beneath ~ 7 km of crust (on average, Nicolas et al 1996) and up to ~
230 20 km of fresh mantle peridotite. Thus, the structural thickness of the ophiolite appears to be at least
231 10 km less than the depth inferred from the high end of the pressure range recorded by the sole
232 (1300 or 1400 MPa, ~ 40 to 45 km). In addition, there is no evidence for widespread, tectonic thinning
233 of the crustal section of the ophiolite, either by faulting or ductile deformation.

234

235 How can these data be reconciled? One possibility is that the peak pressures inferred for the sole are
236 imprecise, and/or that they represent tectonic “overpressures” that don’t correspond closely with
237 depth (Garber et al 2020). In this interpretation, the metamorphism of the sole could have occurred at
238 ~ 800 MPa, corresponding to the current structural thickness of the ophiolite. A second possibility, as
239 noted above, is that the base of the mantle section of the ophiolite underwent tectonic thinning,
240 perhaps via simple shear (Prigent et al 2018a, Soret et al 2017). A third alternative is that some of the
241 lenses of the metamorphic sole – those recording the highest pressures - migrated updip to reach
242 their current structural position, ~ 25 km below the paleo seafloor. Indeed, upward transport of
243 buoyant footwall lithologies during subduction is recorded in many preserved collisional orogens (e.g.,
244 Chemenda et al 2000). If so, updip migration of the sole with respect to the overlying ophiolite must
245 have occurred after peak metamorphism but during Tethyan subduction, prior to emplacement of the
246 ophiolite and the sole over the allochthonous Hawasina sediments. Finally, of course, it is possible
247 that the current juxtaposition of the sole and the base of the ophiolite may be explained as the result
248 of combinations of these three alternatives.

249

250 Subsequent events have affected the wedge, the sole, the underlying sedimentary units, and the
251 faults between them (Grobe et al 2018, Grobe et al 2019). The end of subduction and emplacement
252 of the ophiolite over allochthonous Hawasina sediments and the autochthonous, Arabian continental
253 margin was followed by subaerial erosion, and then by a marine transgression marked by deposition
254 of shallow water limestones at ~ 74 Ma (Al Khirbash 2015, Alsharan & Nasir 1996, Bailey 1981,
255 Hansman et al 2017a, Nolan et al 1990, Schlüter et al 2008, Wyns et al 1992). Then, large scale uplift
256 deformed all these units, forming the gigantic Jebel Akdar and Saih Hatat domes, cored by
257 Proterozoic continental crust (e.g., Glennie et al 1973, Glennie et al 1974b). Saih Hatat uplift and
258 cooling started at about 60 Ma, if not earlier (e.g., Grobe et al 2018, Grobe et al 2019, Hansman et al
259 2017b). Doming reactivated and cut the basal thrust of the ophiolite in normal faults and shear zones.
260 Some of these younger faults juxtaposed mantle peridotite from the ophiolite with the allochthonous
261 Hawasina sedimentary rocks, and even with the autochthonous platform carbonates of the Arabian
262 continental margin, along tectonic contacts where the metamorphic sole is no longer present.

263

264 However, despite these complexities, we reiterate that – where it is parallel to banding and foliation –
265 the contact between the metamorphic sole and the overlying Banded Unit at the base of the Samail
266 ophiolite mantle section represents the basal thrust of the ophiolite. In this paper, when we refer to the
267 “basal thrust”, we are referring to contacts that preserve these characteristics. In turn, though of
268 course there can have been imbrication and/or subduction erosion, the basal thrust of the ophiolite
269 represents the locus of 100’s of kilometers of subduction of oceanic crust, overlying sediments and,
270 ultimately, the Arabian continental margin.

271

272

2.5 Geology of MoD Mountain

273

274 Hole BT1B is on the north side of the wide Wadi Mansah, southeast of “Ministry of Defense
275 Mountain”, (MoD Mountain), which is informally named for the military firing range on the south side of
276 Wadi Mansah. The MoD Mountain region is close to the saddle between the northeastward plunging
277 end of the Jebel Akdar massif, to the west, and the westward plunging Saih Hatat massif to the
278 northeast (Figure 1).

279

280 This region preserves a gently folded, tectonic “stratigraphy” (Figures 2, 3 and 4). The lowest
281 exposed units in this sequence, northeast of Hole BT1B, are diagenetically-altered sedimentary rocks,
282 mostly clastic shales and slates with a few meter to 10 meter scale intercalations of limestone and
283 minor lenses of metavolcanic rocks. These are parts of the Hawasina Formation (Béchenec et al
284 1990, Béchenec et al 1988). Overlying the Hawasina Formation is one of the most aerially extensive
285 outcrops of the metamorphic sole in Oman and the UAE (e.g., Figure 1 and geologic maps in Soret et
286 al 2017, Wilde et al 2002). The outcrop area is unusually large in this region because the unit is
287 regionally flat lying, though broadly folded.

288

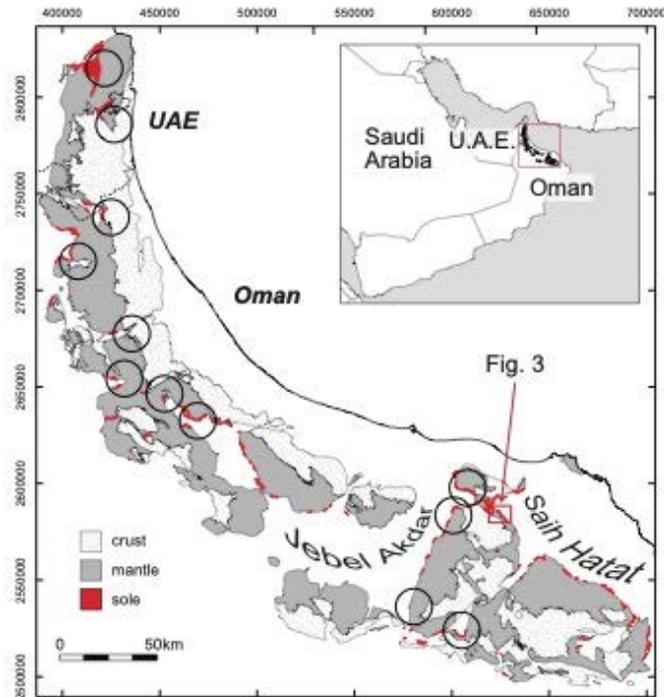


Figure 1: Outcrop area of the Samail ophiolite in Oman and the UAE, based on Nicolas et al. (2000). Metamorphic sole, in red. Black circles indicate approximate location of listvenites (Nasir et al 2007, Stanger 1985, Wilde et al 2002). Red rectangle indicates the approximate location of Figure 3, a geologic map of MoD Mtn and vicinity, which was the site of Oman DP Hole BT1B, and the focus of this paper.

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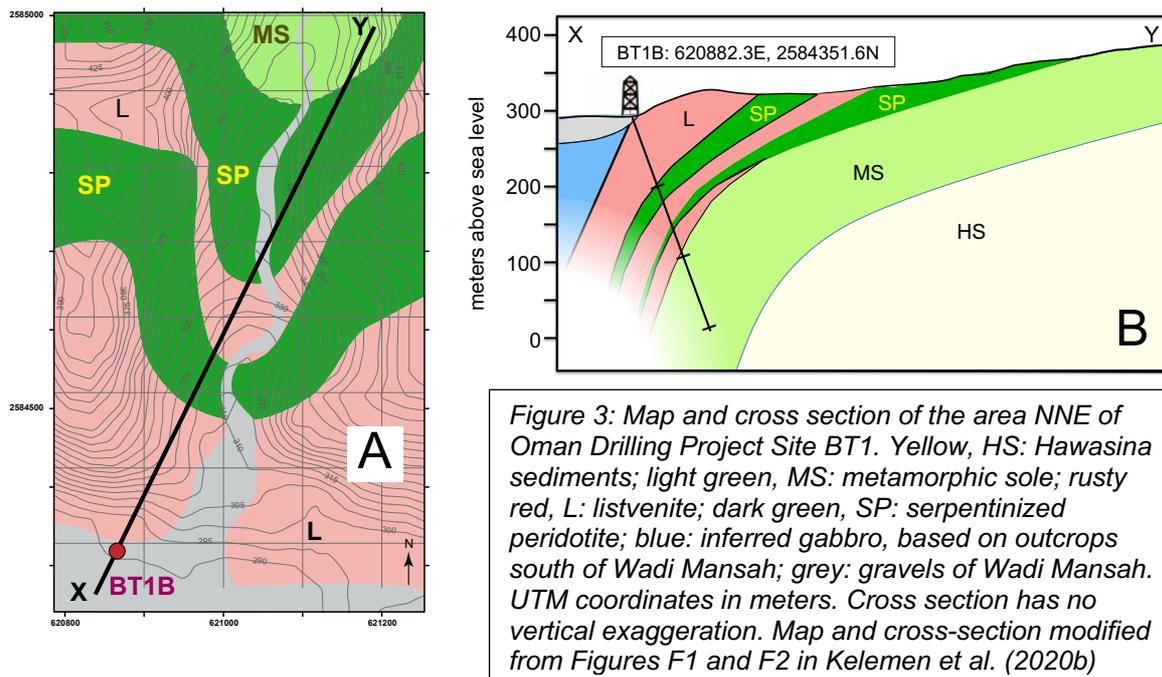
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Figure 2: Photograph of the west end of the MoD Mountain ridge, from the SW, looking NE, showing bands of listvenite (rusty orange) parallel to contacts between partially serpentinized harzburgite (brown) and dunite (tan) comprising the "Banded Unit" at the base of the Samail ophiolite mantle section. Greenish metabasalts and metasediments of the metamorphic sole underlying the ophiolite are exposed along indistinct ridge in lower left. The listvenite band at top right is more than 100 m thick and extends for 1.5 kilometers along the length of the summit ridge. The listvenite band in the center of the photo is 15-20 m thick. Photo taken with a telephoto lens from ~ 23.35°N, 58.17°E, along azimuth ~ 030°.



300
301

302 Above the metamorphic sole in this gently folded “stratigraphy” is partially serpentized peridotite,
 303 composed of distinctive, banded alternations of dunite, harzburgite and lherzolite on a scale of meters
 304 to tens of meters, characteristic of the “Banded Unit” at the base of the ophiolite (Boudier et al 1988,
 305 Boudier & Coleman 1981, Lippard et al 1986, Searle & Cox 2002). Indeed, partially serpentized
 306 mantle peridotites on MoD Mountain, northeast of Hole BT1B have compositions similar to the
 307 Banded Unit elsewhere, and distinct from shallower, residual mantle peridotites of the Samail ophiolite
 308 emantle section, as discussed in [Section 5.5](#), below. The presence of the Banded Unit overlying the
 309 metamorphic sole is another indication that MoD Mountain area exposes the basal thrust of the
 310 ophiolite – the paleo-subduction zone – together with the overlying mantle wedge.

311

312 In some localities, peridotites at the base of the Samail ophiolite mantle section have undergone
 313 100% carbonation at ~ 100-200°C to form “listvenites” (Beinlich et al 2020, Falk & Kelemen 2015,
 314 Glennie et al 1974a, Nasir et al 2007, Stanger 1985, Wilde et al 2002), in which all Mg and Ca are in
 315 carbonate minerals, and silica derived from olivine and pyroxene has formed quartz or chalcedony. In
 316 Oman, such listvenites are most abundant on and around MoD Mountain northeast of Hole BT1B,
 317 where they form part of the gently folded tectonic “stratigraphy” we are discussing here. Listvenites on
 318 the flanks of MoD Mountain form discontinuous tabular lenses with low angle dips, 10 to 200 meters
 319 thick, parallel to the basal thrust and to lithological banding in the peridotite. These lenses occur along
 320 the basal thrust – between peridotite and the sole – and enclosed within the peridotite, up to 300
 321 meters above the sole. Contacts in outcrop between listvenite and the surrounding, partially
 322 serpentized peridotite are marked by strongly foliated, 100% serpentized zones, 1 to > 20 m thick.

323

324 The lithological banding in the peridotite and the listvenite lenses dip gently south on the south side of
 325 MoD Mountain, north on the north slopes of the mountain, and then south again along and NE of the

326 wadi bounding MoD Mountain to the north (Falk and Kelemen 2015 and this paper, [Section 4.2](#)).
327 Despite later faulting, these structures define a broad anticline with an axis approximately coincident
328 with the summit ridge of MoD Mountain, and a syncline with an axis roughly coincident with the wadi
329 northeast of MoD Mountain. Listvenites form erosion resistant dip slopes and the tops of small buttes
330 outlining the folded stratigraphy.

331

332 Listvenites elsewhere in Oman and the UAE are found along the basal thrust, commonly juxtaposed
333 with, or within a few km of, the metamorphic sole and/or the Banded Unit at the base of the Samail
334 mantle section, as at MoD Mountain. In some other outcrops, listvenites form lenses within broad
335 serpentinite mélangé zones at the base of the ophiolite (Nasir et al 2007, Stanger 1985). In contrast,
336 listvenites are not found within the peridotite more than a few kilometers away from the basal thrust of
337 the ophiolite.

338

339 A Rb/Sr isochron on listvenite mineral separates ($97 \text{ Ma} \pm 29 \text{ Ma } 2\sigma$, Falk & Kelemen 2015) is similar
340 to the better determined, 96 to 94 Ma U/Pb ages of zircon in the metamorphic sole and igneous crust
341 in the ophiolite. Based on the listvenite mineral isochron, there is a 67% probability that the listvenites
342 are older than 82.5 Ma (average -1σ), and a 93% probability that they are older than 75 Ma (1.5σ),
343 before the end of subduction. Thus, geological observations (summarized above and in [Section 4.2](#))
344 together with the isochron data indicate that the listvenites formed via transfer of CO_2 and other
345 components from subducting material – probably sediments and/or altered lavas – into the leading
346 edge of the mantle wedge during Tethyan subduction and ophiolite emplacement. New geological
347 data supporting this are presented in 4.2. [Sections 5.6 and 5.7](#) provide thermodynamic modeling that
348 quantifies this hypothesis.

349

350 As noted in [Section 2.4](#), Paleocene to Miocene uplift of the nearby Jebel Akdar and Saih Hatat
351 massifs may have caused reactivation of some older faults, and definitely formed new, younger faults
352 in the MoD area. For example, shallow-level gabbros and sheeted dikes are juxtaposed with mantle
353 peridotite and the metamorphic sole on a steep fault parallel to Wadi Mansah, just south of Hole BT1B
354 (Villey et al 1986, Wilde et al 2002). In another possible example, Scharf et al. (2020) report early
355 U/Pb formation or cooling ages (60 ± 16 and 58 ± 6 Ma) of calcite veins that cut listvenite, cataclasite
356 and fault contacts between listvenite and post-emplacement, Late Cretaceous conglomerates.

357

358

3. Methods

359

360 Here we describe methods used for new data presented for the first time in this paper. [Supplementary](#)
361 [Section S2](#) provides methods for data illustrated in this paper, but previously reported elsewhere.

362

363

3.1 Geological mapping

364 Geological field work to produce the map and cross-section in **Figure 4** spanned short visits over
365 about a decade. Contacts and structural measurements were located by GPS at the time of
366 measurement. The topographic profile for the cross section was constructed using Google Earth.

367

368

3.2 Raman spectroscopy

369

370 Analyses of minerals in thin section and rock slabs were conducted at the Raman Microspectroscopy
371 Laboratory, University of Colorado-Boulder with a Horiba Scientific LabRam HR Evolution Raman
372 microscope. Measurements used a 100 mW 532 nm laser, focused through a 50x (0.75 NA)
373 microscope objective onto a ~2 μm spot. The laser power was modulated with neutral density filters to
374 about 15 mW at the sample surface. Multiple (2-10) accumulations were coadded in order to filter
375 spikes and improve signal to noise, and the acquisition time and accumulation number were adjusted
376 to yield appropriate data quality. Data processing was performed using LabSpec 6 software (Horiba
377 Scientific), including correction for instrumental artifacts and polynomial baseline fitting/subtraction.
378 Raman mapping was performed using a motorized stage with 2 μm step size, and map datasets were
379 fit using classical least-squares fitting with endmember spectra isolated from regions within the map
380 using LabSpec 6 after data processing.

381

382

3.3 Thermodynamic calculations and modeling

383

384 The speciation and chemical mass transfer code EQ3/6 (Wolery 1992) was used to predict the
385 compositions of coexisting solid and aqueous phases that evolved during interaction between
386 representative lithologies from the MoD Mountain area and CO₂-bearing fluids. Thermodynamic data
387 for minerals were mostly from Berman (1988). Data for pyrite and pyrrhotite were from Helgeson et al.
388 (1978). For aqueous species, thermodynamic data used in the simulations were calculated using the
389 Deep Earth Water (DEW) model (Huang & Sverjensky 2019, Sverjensky et al 2014) which uses
390 recent experimental and theoretical advances (Facq et al 2016, Pan et al 2013) to expand the
391 extended Helgeson-Kirkham-Flowers (HKF) aqueous equation of state (Shock et al 1992, Shock et al
392 1997) to pressures up to 6.0 GPa.

393

394 The composition of 5 wt% aqueous fluid in equilibrium with a pelitic lithology from the Oman
395 Hawasina Formation at 400 – 600°C and 0.5 to 2.0 GPa at low water/rock ratios was used.
396 Specifically, a dilute fluid was equilibrated with the rock composition of sample OM20-17 (de Obeso et
397 al 2021a), containing 0.06 wt% total carbon (**Supplementary Table 2**). The CaO content of OM20-17
398 was below detection. For the model calculations it was assumed to 0.1 wt%. In addition, the S content
399 of this sample has not been measured. For this calculation it was assumed 100 ppm. At these high
400 temperatures and low carbon contents, carbonate minerals are unstable and all carbon in the rock will
401 be mobilized into the fluid phase as dissolved CO₂.

402

403 We calculated the outcome of cooling and decompression of the CO₂-rich fluid from OM20-17, to 100
404 – 300 °C and 0.5 to 2.0 GPa. This had no significant effect on its composition. We then calculated the
405 products of reaction between this fluid and average Oman harzburgite (Supplementary Table 2,
406 calculated from Godard et al 2000, Hanghoj et al 2010, Monnier et al 2006) at 100 – 300 °C and 0.5 –
407 1.0 GPa, at water:rock ratios ranging from 100 to 1.

408

409 As a result of data limitations, solid solutions of precipitating minerals were not considered, as the
410 Berman database lacks properties for most Fe-endmembers of minerals commonly observed in
411 listvenites and associated rocks. Thus, for example, the model predicts co-precipitation of pure,
412 endmember magnesite, dolomite and siderite, whereas in listvenite samples we observe Fe-bearing
413 magnesite and dolomite. Among the serpentine polytypes, only chrysotile precipitation can be
414 modeled. We did not include goethite. There are no thermodynamic data for a chromian muscovite
415 component, so this was not included, despite the fact that solid solutions ranging from fuchsite to
416 chromian muscovite are observed in MoD Mountain listvenites (e.g., Falk & Kelemen 2015).

417

418 Phase equilibrium calculations constraining the conditions for co-existing graphite (\pm amorphous
419 carbon compounds) and hematite, and updated calculations for co-existing antigorite and quartz,
420 used (1) Thermocalc (Powell et al 1998), (2) Perple_X (<https://www.perplex.ethz.ch/>) (Connolly 1990,
421 Connolly 2005, Connolly 2009), with the Holland and Powell thermodynamic data for minerals (2003,
422 1998), and the default equations of state for H₂O- CO₂ fluids (modified versions of Redlich-Kwong),
423 and (3) SUPCRT (Johnson et al 1992, Zimmer et al 2016) with thermodynamic data for minerals from
424 Helgeson et al. (Helgeson 1985, 1978) or Berman (1988, plus graphite from Helgeson et al.) and
425 various equations of state for H₂O-CO₂ fluids (Shock et al 1992, Shock et al 1997) modified from
426 Helgeson et al. (1981). All of these different combinations provided consistent results, with antigorite
427 + quartz stable with respect to talc at temperatures up to 80 to 120°C. However, calculations using
428 the Deep Earth Water (DEW) model (Huang & Sverjensky 2019, Sverjensky et al 2014) and the
429 extended Helgeson-Kirkham-Flowers (HKF) aqueous equation of state (Shock et al 1992, Shock et al
430 1997) do not predict equilibrium coexistence of antigorite + quartz above 15°C.

431

432 3.4 (U,Th)/He ratio measurements and cooling age calculation

433

434 All (U-Th)/He analyses were completed at the UTChron facility at the University of Texas at Austin,
435 using aliquots of zircon separates from the metamorphic sole and lower crustal gabbros, previously
436 analyzed for U/Pb ages by Rioux et al. (in prep.), following procedures of Wolf and Stockli (2010).
437 Individual zircon grains were morphometrically characterized to determine alpha ejection correction
438 (Ft, Farley et al., 1996; Cooperdock et al., 2020), equivalent spherical radius (ESR), and estimated
439 mass assuming a tetragonal prism. Single-grain zircon sample aliquots were loaded into Pt tubes for
440 in-vacuo laser He heating for 10 min at ~1200°C by diode laser and ⁴He concentrations were
441 measured by isotope dilution, using a ³He tracer, on a Blazers Prisma QMS-200 quadrupole mass
442 spectrometer, after cryogenic purification. Blanks and ⁴He gas standards were run between unknowns

443 to monitor and quantify the procedural baseline during analytical runs. Aliquot laser reheating was
444 repeated (2-5x) until 4He gas yields dropped <1% total extracted gas.

445

446 After degassing, individual zircon grains were removed from the Pt packets and dissolved using a
447 two-step HF-HNO₃ and HCl pressure vessel dissolution technique and measured on a Thermo
448 Element2 HR-ICP-MS following the procedure outlined in Wolf and Stockli (2010). U-Th-Sm
449 concentrations were calculated using isotope dilution with an isotopically enriched, mixed U-Th-Sm
450 spike calibrated against a 1 ppb U-Th-Sm gravimetric standard solution and blank-corrected using the
451 average of multiple procedural blanks.

452

453 Final (U-Th)/He ages were calculated using blank corrected U, Th, Sm and He measurements for
454 each aliquot. Reported concentrations were determined using the morphometrically determined mass
455 of each aliquot. The reported error for individual (U-Th)/He ages represents standard error (8%)
456 based on long-term intra-laboratory reproducibility of Fish Canyon tuff zircon standard, following the
457 approach of Farley et al. (2001). The reported mean sample ages reflect the arithmetic mean of the
458 aliquot ages and their standard deviations.

459

460 3.5 Calibration of XRF core scanner data

461

462 XRF core scanner data were collected onboard DV Chikyu, as described in Kelemen et al. (2020b).
463 We used the core scanner to analyze nine listvenite samples from BT1B core, and 14 gabbro
464 samples from Hole GT1A core that had known bulk compositions based on XRF analysis at the
465 University of St. Andrews. While onboard DV Chikyu, we used the St. Andrews data to calibrate the
466 XRF data, as follows: wt% SiO₂ = 0.89 x (scanner wt% SiO₂); wt% MgO = 2.57 + 1.18 x (scanner wt%
467 MgO); wt% FeO^T = 1.048 + (scanner wt% FeO^T)^{0.848}; and wt% CaO = 0.878 x (scanner wt% CaO),
468 where FeO^T indicates all Fe is treated as FeO. Fits are illustrated in [Supplementary Figure 2](#). Okazaki
469 et al. (2021) present a comprehensive analysis of the XRF scanner data, together with X-Ray
470 tomography data for BT1B core.

471

472 3.6 Calculation of mineral volume proportions

473

474 Volume proportions of quartz, magnesite and dolomite were estimated from bulk rock compositions
475 and XRF scanner data as follows. Weight fractions of SiO₂, MgO, FeO^T and CaO were converted to
476 moles in 100 grams of rock using their molecular weights. (For all data reported in this paper, the sum
477 of wt% SiO₂, MgO, FeO^T and CaO was greater than 90% of the volatile free, bulk rock composition).
478 The number of moles of dolomite were taken to be equal to moles of CaO, moles of magnesite were
479 calculated as moles MgO – moles CaO, and moles of quartz were taken to be equal to moles of SiO₂.
480 All Fe was inferred to be in Fe-oxides and hydroxides. If the small amounts of Fe in carbonate
481 minerals were included in such a calculation, this would slightly increase the proportions of magnesite
482 and dolomite, relative to quartz. Volumes of each mineral in 100 grams of rock were calculated using

483 their molar volumes. The data were “projected” from Fe oxy-hydroxides by normalizing the volumes of
484 quartz, magnesite and dolomite to 100%.

485

486

4. Results

487

488

4.1 Drilling operations

489

490 Site BT1 is on the north side of the broad channel of Wadi Mansah, which drains mountainous
491 regions to the east and southeast. Hole BT1A penetrated 1.90 meters of gravels in Wadi Mansah,
492 south of listvenite outcrops flanking the Wadi. After we became concerned that a steep hole there
493 might intersect tens of meters of gravel before reaching bedrock, and/or that the gravel might overlie a
494 major, steep fault along Wadi Mansah that postdates ophiolite emplacement, we moved the drill and
495 inclined the Hole. Hole BT1B is three or four meters closer to the listvenite outcrop. The well head is
496 intact, marked and protected from floods by a concrete monument. Drilling of the fine-grained, silica-
497 rich listvenites was challenging, because this lithology has a hardness similar to fine-grained chert or
498 flint (~ 7 on the Mohs’ scale), but with patience and expert drilling, we obtained ~ 100% recovery of all
499 lithologies intersected by the borehole. Details of drilling operations are in Kelemen et al. (2020b).

500

501

4.2 Mapping and structural observations

502

503 Geological mapping of the area around MoD Mountain, together with measurement of the orientation
504 of lithological contacts, began in 2009, and continued via brief visits through 2019. As noted in
505 [Section 2.5](#), and reported by Falk and Kelemen (2015), the mountain is underlain by a southeast to
506 northwest striking anticline, with its faulted hinge approximately coincident with the ridge along the
507 summit. Exposed contacts between listvenite and serpentized harzburgite consistently dip to the
508 southwest on the southwest side of the mountain, and to the east and northeast on the northeast side.
509 In the valley north of the mountain, listvenite-harzburgite, listvenite-metamorphic sole, and
510 harzburgite-sole contacts form a broad, shallow syncline. A new, detailed geological map and cross-
511 section, incorporating our lithological and structural observations, is presented in [Figure 4](#).

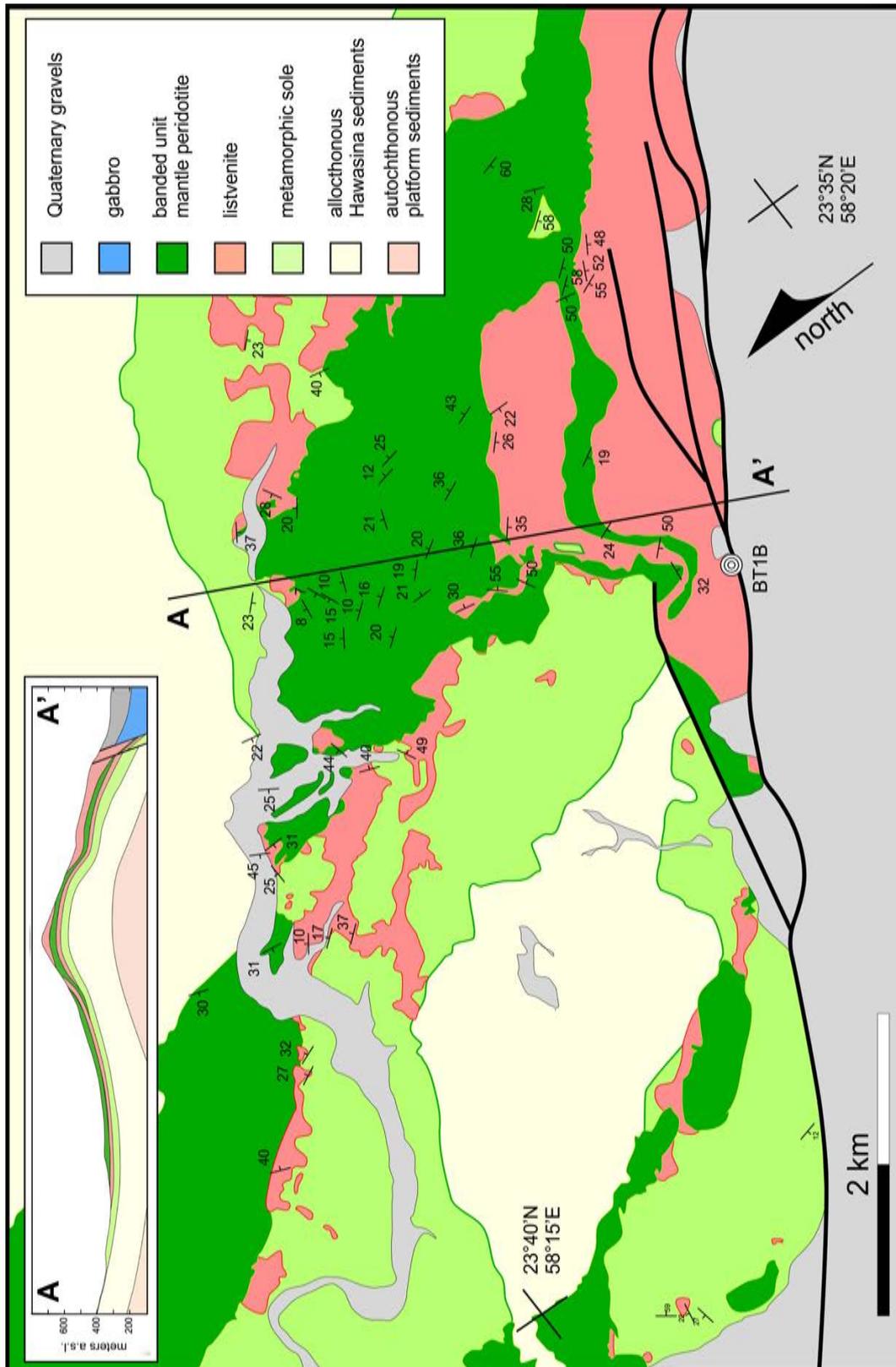
512

513 As shown on the map, in outcrops extending for more than 4 km north of Hole BT1B there is a regular
514 tectonic “stratigraphy”, with variably altered peridotite overlying the metamorphic sole, in turn
515 overlying Hawasina Formation sediments, all with low angle fault contacts that have been deformed
516 by a series of gentle, broad open folds evident in the map and cross-section.

517

518 We noted normal and reverse shear sense indicators on both sides of the anticline. As a result of the
519 folding, it is difficult to interpret the sense of shear recorded in various outcrops. Some shear sense
520 indicators may predate the folding, while others may record deformation during or after folding.

521



522

523 *Figure 4: Geologic map and cross section of MoD Mountain and vicinity. Complex map pattern arises*
 524 *from intersection of topography with broadly folded, gently dipping units, as is more evident in the*
 525 *cross section (no vertical exaggeration) illustrating the antiform coinciding with MoD Mountain, and*
 526 *the syncline to its north. Dips are all measured on lithologic contacts, including dunite/harzburgite*
 527 *contacts within the Samail ophiolite mantle section.*

528

529 In contrast, to the northwest and southeast, outside our map area, the outcrop patterns become much
530 more complex, the sole outcrop thins, and there are some vertical fault contacts where all of these
531 older units are juxtaposed with Late Cretaceous Al Khod conglomerates and younger, shallow marine
532 limestones (Stanger 1985, Villey et al 1986, Wilde et al 2002).

533

534

4.3 Zircon (U,Th)/He cooling ages

535

536 Zircon (U,Th)/He cooling ages on samples from the metamorphic sole southeast of Fanjah, near MoD
537 Mountain, are 38.7 ± 7.7 and 44.4 ± 8.0 Ma, cooling ages of zircons from the metamorphic sole at the
538 base of the Wadi Tayin massif to the east are 54.5 ± 7.4 and 61.8 ± 2.6 Ma, and the cooling age of
539 zircons from the lower crust of the Samail massif is 46.4 ± 3.9 Ma (Supplementary Table 1 and
540 Supplementary Figure 1).

541

542

4.4 Lithology

543

544 As illustrated in Figure 5, the top of the Hole sampled ~ 200 meters of listvenite interlayered with two
545 serpentinite bands from 80 to 100 m depth, and 181 to 185 m depth. Below 185 m, the listvenite is
546 ubiquitously deformed, with visual core descriptions indicating a mixture of brittle and ductile
547 deformation. At about 197 m, core was composed of a few tens of cm of soft, clay-rich fault gouge,
548 together with a few cm of hard, aphanitic, black ultracataclasite. Beneath these fault lithologies, the
549 core sampled ~ 102 meters of the metamorphic sole, grading from dominantly fine-grained, finely-
550 banded, muscovite-bearing metasediments at the top ("greenschists" in Figure 5) to coarser, more
551 massive-appearing, foliated "greenstones", interpreted as metavolcanic rocks, at the bottom.

552

553 Serpentinite bands in the core have gradational contacts with host listvenites over 10's of centimeters
554 to ~ 1 m thick. Serpentinities contain antitaxial veins of magnesite with a median line composed of
555 hematite and other Fe-oxides. There are prismatic terminations of magnesite crystals away from vein
556 centers, toward the host serpentine (Figure 6). Antitaxial veins record growth of minerals outward
557 from the vein center. They are commonly interpreted to open due to the "pressure of crystallization"
558 (Durney & Ramsay 1973, Urai et al 1991). However, this interpretation is less clear in the
559 serpentinites and listvenites of Hole BT1B, where the Mg in the carbonate is derived from the host
560 rocks. To some degree these veins may replace, rather than displace, the host.

561

562 Away from the veins, serpentinites also contain up to 10% magnesite ovoids 10 to 100 microns in
563 diameter, unevenly dispersed within a massive serpentine matrix. These magnesite vein and ovoid
564 textures are abundant in the listvenites as well. Thus, the Shipboard Scientific Party suggested that
565 they are indicative of incipient replacement of serpentinite by listvenite, grading from < 10% carbonate
566 (and no quartz) in veins and ovoids to 100% fine-grained carbonate + quartz across sharp reaction
567 fronts (Kelemen et al 2020b). Another notable feature is that some of the serpentinites are optically

568 isotropic in thin section, probably indicative of low temperature formation of poorly ordered or
 569 amorphous material with serpentine stoichiometry (e.g., Andreani et al 2004).
 570

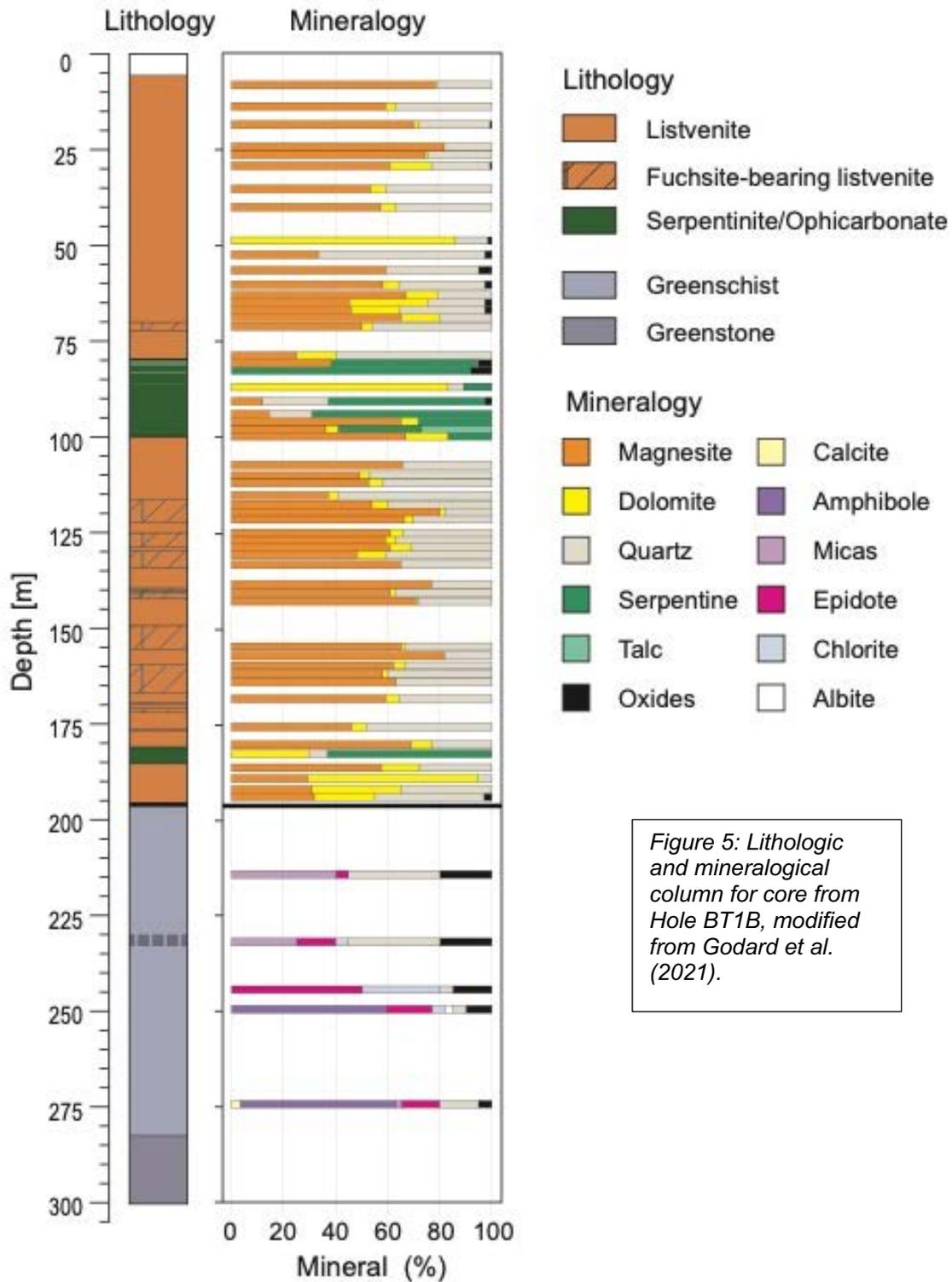
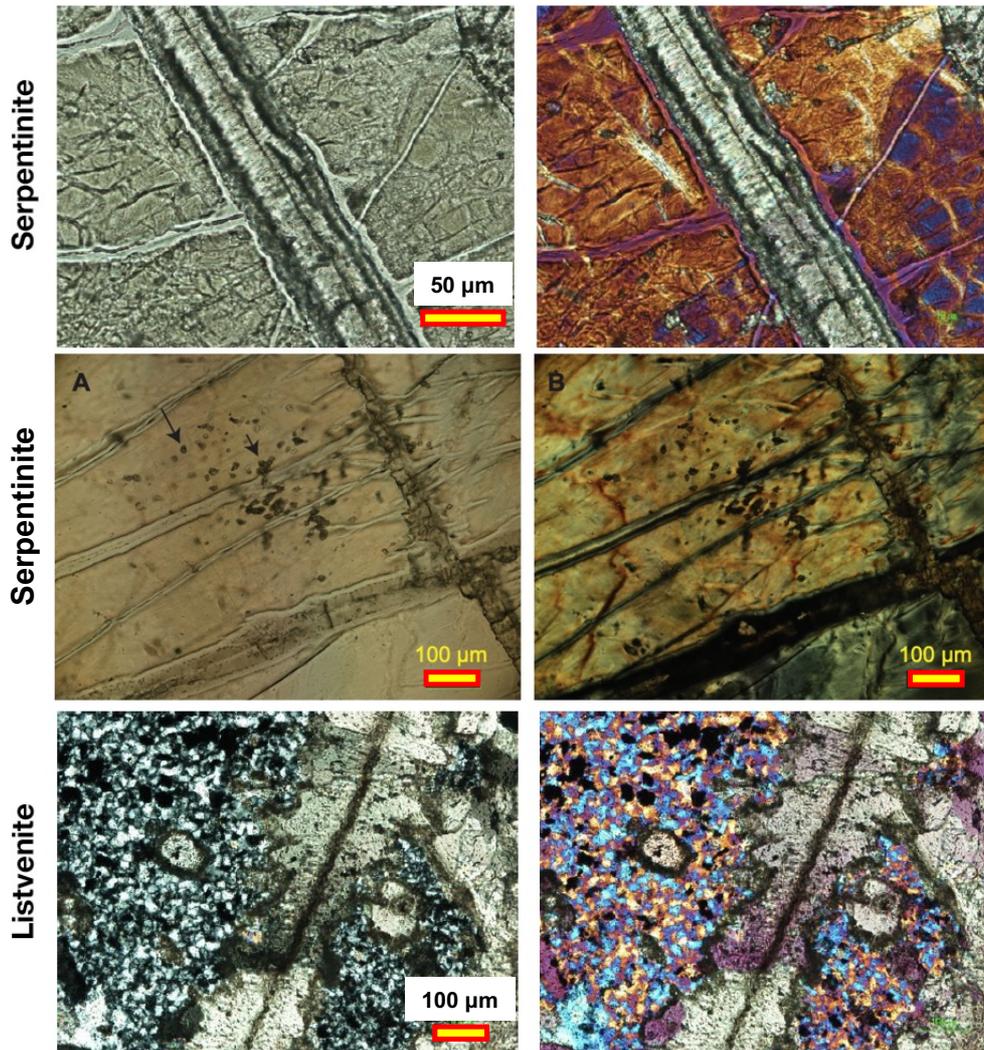


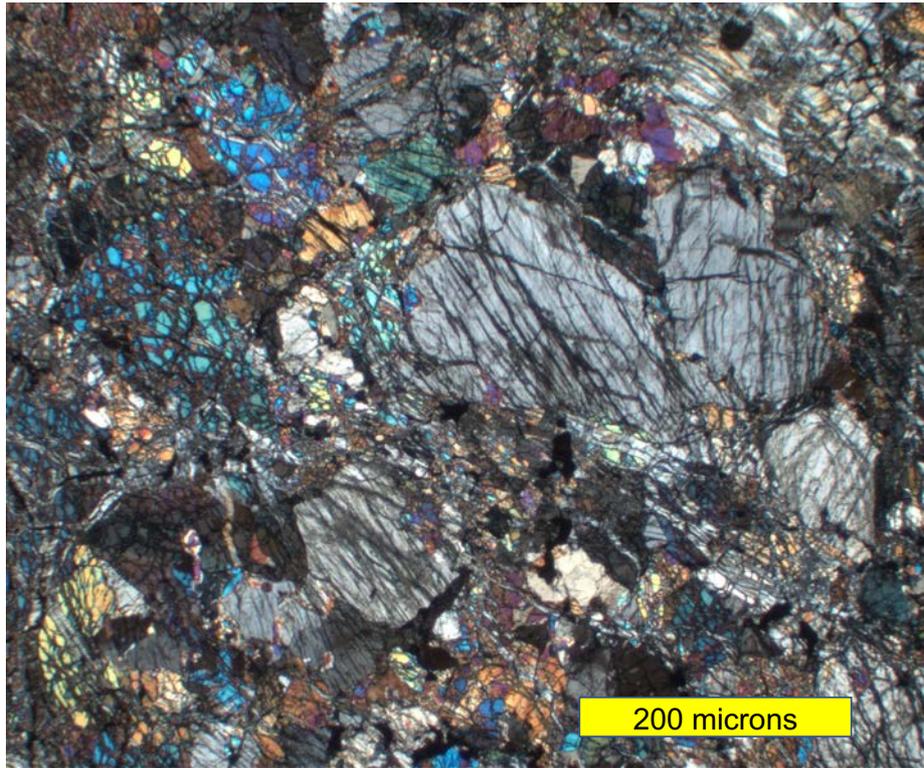
Figure 5: Lithologic and mineralogical column for core from Hole BT1B, modified from Godard et al. (2021).

571
 572
 573



574
 575 *Figure 6: Antitaxial magnesite-hematite veins, and magnesite spheroids in serpentinites and*
 576 *listvenites in core from Hole BT1B. Top panels: plane light (left) and crossed-polarized images (right,*
 577 *quartz plate (+1λ) inserted) of magnesite-hematite veins near the lower contact of the upper*
 578 *serpentine band, TS_BT1B_44Z-3_9-11.5, ~100 m depth, from Figure F47 in Kelemen et al.*
 579 *(2020b). Middle panels: tiny magnesite spheroids in serpentine, TS_BT1B_44Z-3_9-11.5, ~100 m*
 580 *depth, from Figure F29 in Kelemen et al. (2020b). F. Bottom panels: Cross-polarized images, right*
 581 *one with quartz plate (+1λ) inserted, of texturally similar, “antitaxial” magnesite-hematite veins and*
 582 *magnesite ovoids in quartz-rich, listvenite matrix, TS_BT1B_47Z-3_15-19 at about 110 m depth, from*
 583 *Figure F35 in Kelemen et al. (2020b).*
 584

585 In turn, listvenites and serpentinites recovered in drill core are hosted by more typical, partially
 586 serpentinized peridotites and dunites in outcrop north and northeast of Hole BT1B (Figure 7). Such
 587 lithologies, typical of the Banded Unit at the base of the mantle section of the Samail ophiolite, are
 588 abundant on the flanks of MoD Mountain, and are particularly well exposed west of the summit
 589 (Figure 2) and on the broad, north facing outcrop below the summit ridge.
 590



591
592 *Figure 7: Cross-polarized image of partially-serpentinized harzburgite sample OM09-14 (Falk &*
593 *Kelemen 2015) from ~ 10 m above lower listvenite band in Figure 2. Olivine: bright interference colors*
594 *and irregular, serpentine-filled fractures. Orthopyroxene: grey interference colors and parallel to*
595 *orthogonal fractures. Minor calcic-pyroxene and/or hornblende are barely visible in this image.*
596

597 A sample transect on the ridge forming the drainage divide between Wadi Mansah (site of Hole BT1B)
598 and the parallel wadi north of MoD Mountain documented a 5-meter scale progression from listvenite
599 to serpentinite (with intergrown quartz and antigorite) to partially serpentinized peridotite containing
600 relict olivine and orthopyroxene (Figure 5 in Falk & Kelemen 2015). Along that watershed transect, the
601 presence of antigorite – rather than the serpentine polytypes lizardite and chrysotile – was attributed
602 to high SiO₂-activity produced by reaction of olivine and serpentine to produce carbonate and quartz,
603 since antigorite is more SiO₂-rich than the other polytypes.

604
605 However, the serpentinites in core from Hole BT1B are distinct from the serpentinized zone flanking
606 listvenite on the ridge transect, and from the surrounding, partially serpentinized Banded Horizon
607 harzburgites. Although quartz veins cut the serpentinite in the core, antigorite was not observed.
608 Moreover, despite the presence of some orthopyroxene pseudomorphs (“bastites”) in serpentinites,
609 and a concerted effort to find relict mantle minerals, no olivine or pyroxene were detected in drill core.
610 Taken together, field and core observations suggest that the contact between serpentinites and
611 partially serpentinized peridotites is gradational over a few meters at most, approximately as sharp as
612 the contact between listvenites and serpentinites. More on this in Sections 5.7 and 5.8, below.

613
614 Essentially, two types of listvenite were recovered, magnesite + quartz + iron oxide lithologies, and
615 volumetrically less abundant, dolomite + quartz + iron oxide rocks, previously termed magnesite-

616 listvenites and dolomite-listvenites (Falk & Kelemen 2015). Much of the core contains 0.5 to 3% relict
617 chromian spinel, partially or fully altered to Fe-oxides. Instead or in addition, some samples contain
618 minor amounts of Cr-rich white mica (fuchsite-muscovite solid solutions, supplementary Figure 7 in
619 Falk & Kelemen 2015), in mm to cm scale, ovoid, microscopic intergrowths with quartz. These
620 intergrowths are macroscopically evident in outcrop and core as cm-scale green spots, though in fact
621 Cr-rich mica composes only a few percent of such spots, apparently has undergone alteration to clays
622 in some samples, and was significantly damaged or removed during thin section preparation. As a
623 result, fuchsite crystals recovered from BT1B core are not large enough for $^{40}\text{Ar}/^{39}\text{Ar}$ analyses. Figure
624 5 of Nasir et al. (2007) is a photomicrograph of crystalline fuchsite from another listvenite in Oman.

625

626 Macroscopic listvenite textures are characterized by abundant veins (10 to 200 veins more than 1 mm
627 thick per meter of core, typically ~ 1 per cm) in a fine-grained matrix. In massive listvenites, the fine-
628 grained matrix surrounding veins commonly contains ovoids of magnesite or quartz (Figure 8).
629 Though they have similar textures, ovoids of the two different minerals are rarely adjacent to each
630 other. Both commonly have Fe-oxides in their cores and/or in spherical zones. Microprobe analyses
631 show that magnesite ovoids have low Fe cores, commonly rimmed with relatively Fe-rich magnesite
632 (Beinlich et al 2020). They have sizes and shapes similar to the quartz spherulites.

633

634 Carbonate ovoids and cross-cutting magnesite-hematite veins are also observed in serpentinite
635 bands in the core (Figure 6). Thus, the Shipboard Science Party considered it likely that many such
636 veins initially formed within serpentinite, followed by formation of ovoids within surrounding
637 serpentine, and then by replacement of the entire serpentinite matrix by carbonate + quartz (Kelemen
638 et al 2020b). If so, in contrast to conventional interpretations of veins as relatively young features,
639 “cross-cutting” their matrices, in this case the fine-grained listvenite matrix may postdate the earliest
640 veins found within the matrix. This hypothesis is discussed further in Section 5.9

641

642 The quartz ovoids have the texture of “spherulites”, with radiating microscopic crystals producing a
643 false, “uniaxial interference pattern” in cross-polarized light. Spherulites form during devitrification of
644 amorphous opal as well as rhyolite glass, so Falk & Kelemen (2015) and the Shipboard Science Party
645 (Kelemen et al 2020b) interpreted these as replacing opal, which would have been among the earliest
646 SiO_2 minerals to form in many of the listvenites. Importantly, opal is commonly found in other
647 listvenites and serpentine-magnesite associations worldwide (Abu-Jaber & Kimberley 1992, Aftabi &
648 Zarrinkoub 2013, Akbulut et al 2006, Arisi Rota et al 1971, Barnes et al 1973, Beinlich et al 2010,
649 Borojević Šoštarić et al 2014, Boschi et al 2009, Ece et al 2005, Jurković et al 2012, Lacinska &
650 Styles 2013, Lapham 1961, Oskierski et al 2013a, Oskierski et al 2013b, Posukhova et al 2013,
651 Quesnel et al 2016, Searston 1998, Ulrich et al 2014, Zarrinkoub et al 2005).

652

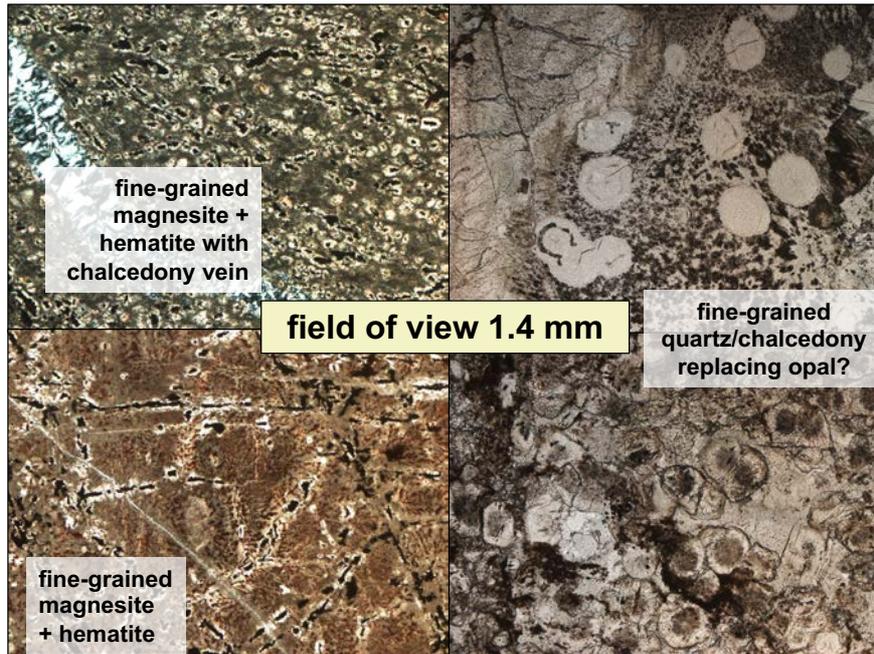
653 Vein types cutting this fine-grained matrix generally record a progression from texturally early,
654 antitaxial magnesite veins – some with cores of hematite + other Fe-oxides (Figure 6) – and related,
655 early Fe-oxide veins, to syntaxial dolomite veins and carbonate-quartz veins, and lastly to syntaxial

656 calcite veins. Some of the late, syntaxial veins contain vugs lined with prismatic calcite and/or
657 dolomite. Syntaxial vein textures record inward crystallization of crystals into fractures that opened
658 due to external, tensional stresses (Durney & Ramsay 1973, Urai et al 1991).

659

660 (A poorly exposed, weathered, fuchsite vein has been observed in outcrop 200 meters north of Site
661 BT1B, but no such veins were sampled in BT1B core. We mention this simply to emphasize that Cr
662 and Al were mobile at some stage during listvenite formation or later alteration.)

663

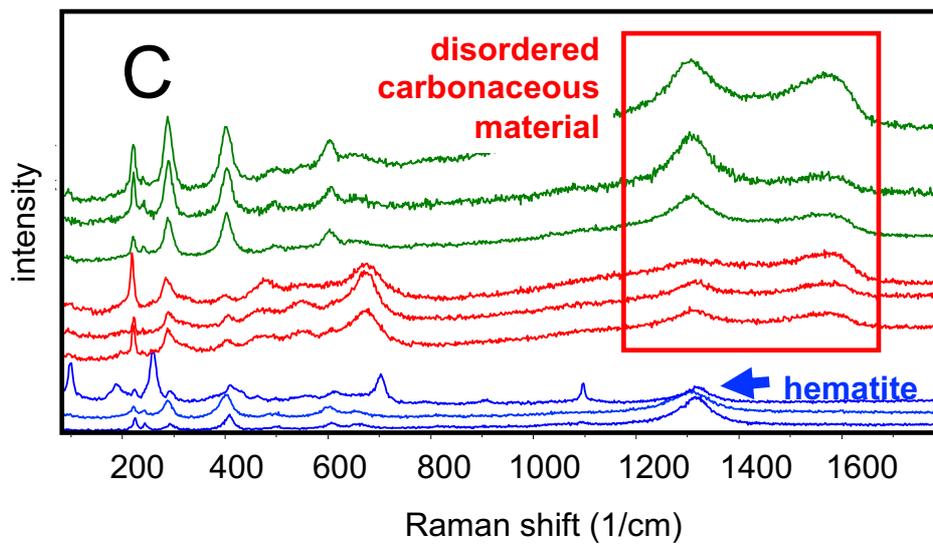
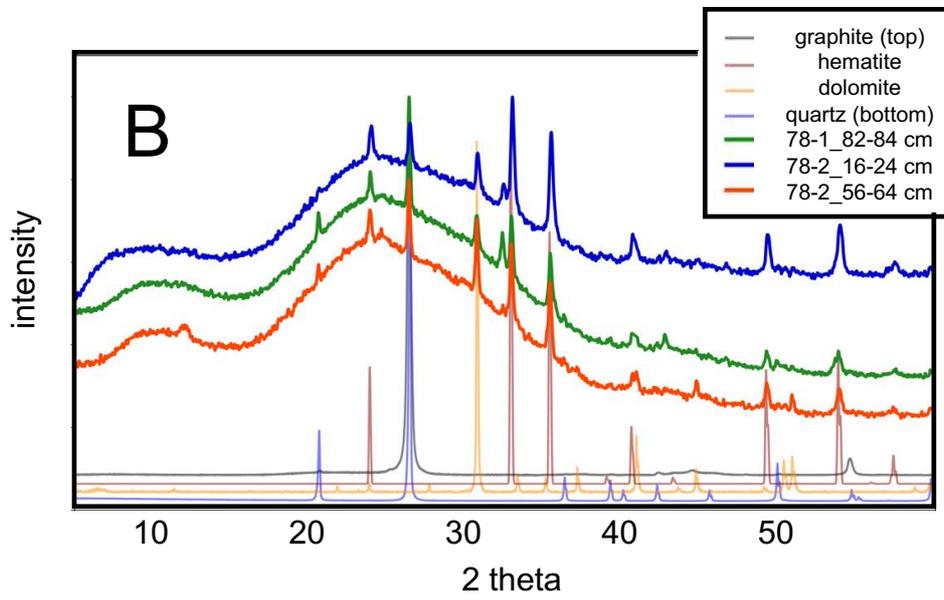


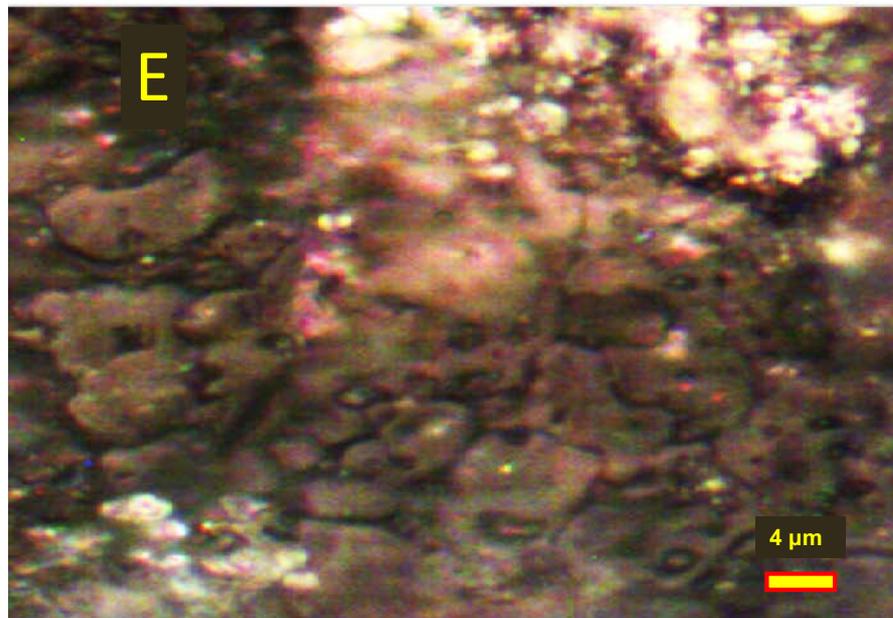
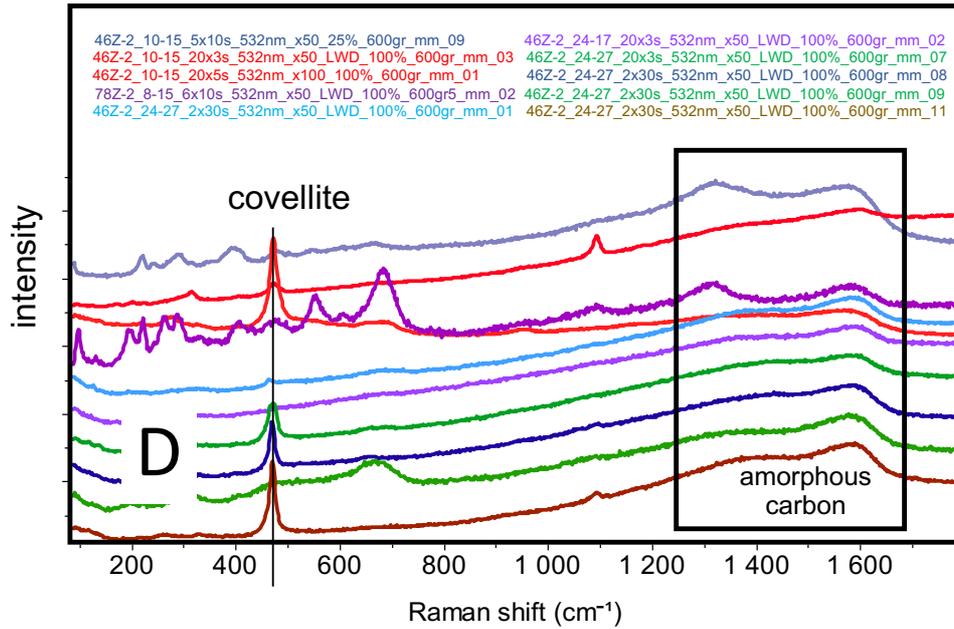
664

665 *Figure 8: Plane light photomicrographs illustrating magnesite ovoids in a matrix composed of*
666 *magnesite, quartz, and subordinate hematite and Fe-oxyhydroxides, TS_BT1B_20Z-1_42-46, ~ 40 m*
667 *depth (left top) and TS_BT1B_27Z-2_6-8.5, ~ 59 m depth (left bottom), and quartz spherulites with*
668 *carbonate and hematite inclusions, in matrix of fine-grained quartz and hematite with subordinate,*
669 *microscopic carbonates, TS_BT1B_60Z-1_12-17, ~140 m depth (right).*

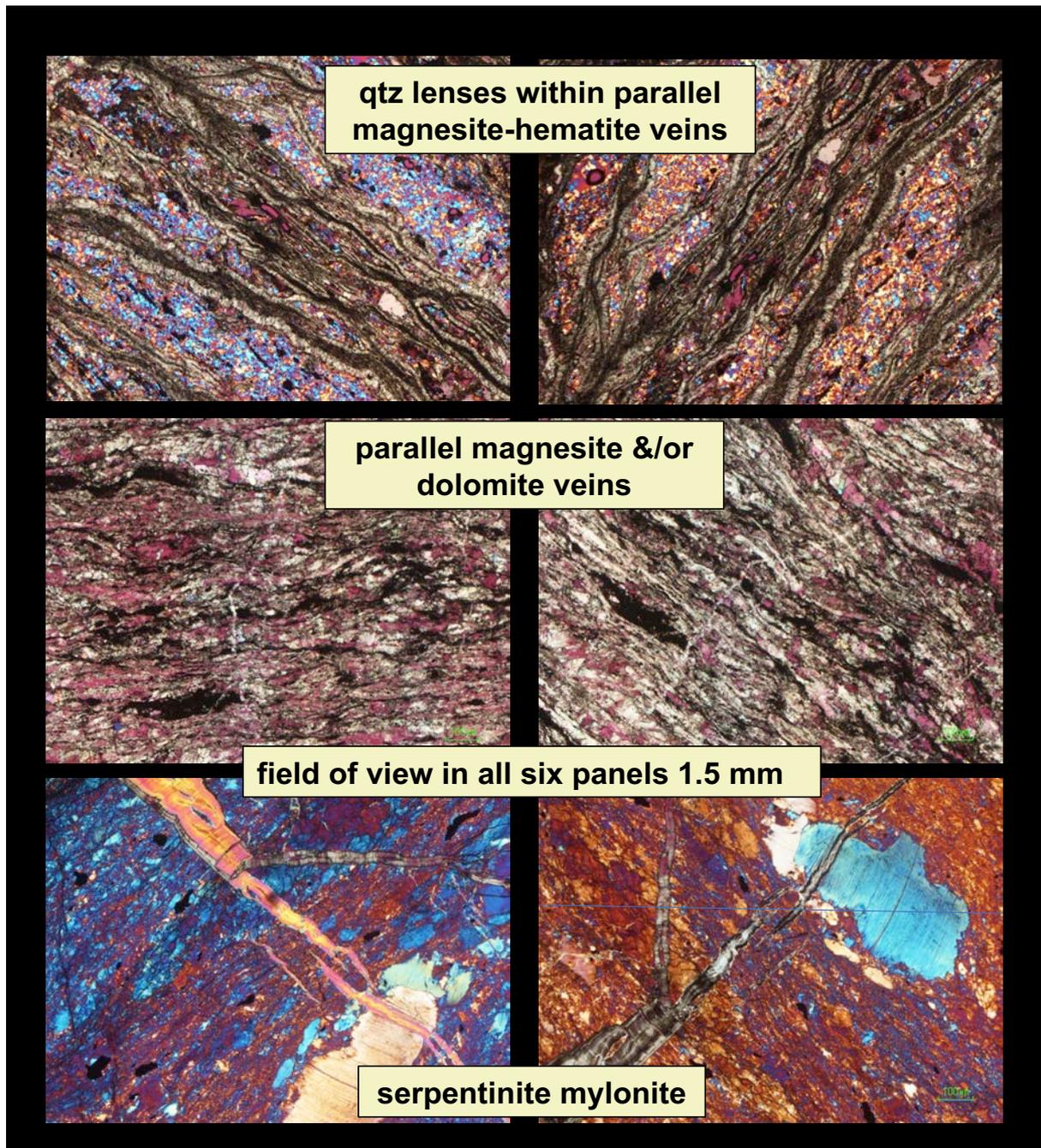
670

671 Among the Fe-oxide veins, some contain minor sulfide – generally not detected during core
672 description – and amorphous, organic carbon compounds. The carbon compounds were first
673 identified in core at the drill site, in the lowest listvenite band, as elongate lenses within transposed
674 hematite veins parallel to the penetrative foliation, where they were described as “graphite”. Soft
675 organic carbon compounds in these features appear to have been largely lost from sample surfaces
676 during washing and handling of the core prior to shipboard observations and analyses, and again
677 during fabrication of thin sections. However, Raman spectroscopy of small, armored relicts, in oxide
678 veins and also in isolated, dark red spots that resemble relict spinel on the core face and rock slabs,
679 reveals the presence of disordered, thermally immature carbonaceous material (Figure 9), some of
680 which may retain a more ordered organic molecular structure. The carbonaceous materials we can
681 still find, on freshly cut surfaces from the core interior, are commonly on the margins of microscopic
682 chalcocite and covellite crystals, in one case also associated with copper sulfate (chalcantite)





684
 685 *Figure 9: Carbonaceous material in drill core. A: Drill site photo of 1 to 2 mm vein of shiny, grey, soft*
 686 *material described as graphite on the drill site, in a vein rimmed with hematite. Field of view 5 cm*
 687 *wide, core 74Z-01, ~ 195 m depth. B: Shipboard XRD spectra of soft “graphite” powder extracted from*
 688 *veins with “graphite” + hematite, replacing Figure F43 in Kelemen et al. (2020b). Interpretation of*
 689 *these data is complicated by the similarity of the quartz and graphite peaks at ~ 26° 2θ, but quartz*
 690 *also has a prominent peak at ~ 21° 2θ which is absent from the blue spectrum for 78Z-02_16-24. C:*
 691 *Raman spectra of black material in samples BT1B_77Z-03_30-38 (blue), 78Z-02_8-15 (red) and 78Z-*
 692 *02_50-56 (green, ~ 192-198 m depth). Broad double peaks at wavenumbers of ~1350/cm and*
 693 *1600/cm are indicative of disordered carbon compounds; no Raman spectra diagnostic of graphite*
 694 *were obtained. Many microscopic, soft, black domains contained hematite, with a single broad peak*
 695 *at ~1350/cm, instead of, or in addition to, disordered carbon compounds. D: Raman spectra of black*
 696 *material in samples BT1_44Z-02_10-15, BT1_78Z-02_8-15, and BT1_44Z-02_24-27, showing broad,*
 697 *double peaks indicative of disordered carbon compounds, some associated with covellite. Core 44Z ~*
 698 *98 m depth. E: dark grey copper sulfate “cow pies”, spatially associated with brightly reflecting*
 699 *covellite, near amorphous carbon material, field of view ~ 100 microns, sample BT1_44Z-02_24-27.*
 700 *Data and images from core 44Z are from a 1 mm diameter black spot with a red rim in the interior of*
 701 *the core, exposed by the rock saw during sample preparation.*



702

703 *Figure 10: Examples of crystallographic preferred orientation (CPO) in localized zones in core from*
 704 *Hole BT1B. All images in cross-polarized light with quartz plate inserted. Images on right are of the*
 705 *same area as on left, but rotated 90° with respect to the polarizers. Areas showing optical continuity*
 706 *have a crystallographic preferred orientation. Top, TS_BT1B_31Z-4_12-14, ~ 65 m depth, quartz*
 707 *lenses within sub-parallel, anastomosing magnesite-hematite veins. Middle, TS_BT1B_78Z-2_34-38,*
 708 *~ 195 m, thin section composed almost entirely of parallel magnesite and/or dolomite veins, with a*
 709 *CPO in the carbonates. Bottom, TS_BT1B_74Z-1_59-62, ~ 183 m, serpentinite mylonite, with a*
 710 *strong CPO in the fine-grained matrix, and visible, internal deformation in serpentine porphyroclasts.*
 711

712

4.5 Crystallographic preferred orientation of minerals

713

714 An overall preferred orientation of veins is not evident from structural data on the core scale, possibly
 715 due to differential rotation of core pieces. And, systematic measurements have not been made on the

716 outcrop scale. However, at the meter scale many core intervals contain textures indicative of ductile
717 deformation (Figure 10). Some samples show a strong macroscopic foliation, defined by parallel
718 (possibly transposed) veins enclosing elongate lenses of the fine-grained matrix, in textures
719 commonly interpreted to form via boudinage during ductile deformation. In samples with a strong
720 foliation defined by dozens of subparallel, early magnesite veins per 10 mm², intervening patches of
721 fine-grained quartz commonly have a crystallographic preferred orientation (CPO). Some samples
722 with a strong foliation defined by abundant, subparallel (tectonically transposed?) carbonate veins
723 also have an optically evident, crystallographic preferred orientation in magnesite and/or dolomite.
724 Similarly, some shear zones in serpentinite have an optically evident, strong shape- and
725 crystallographic-preferred orientation of lizardite crystals, and contain deformed serpentine
726 porphyroclasts.

727

728 *4.6 Brittle deformation textures*

729

730 A broad range of different breccias and cataclasites are observed in listvenites and in the
731 metamorphic sole, in outcrop and in core. In turn these are cut by sharp faults – some associated with
732 planar bands and branching veins of aphanitic ultracataclasite and/or pseudotachylite – and by late
733 calcite veins. The nature and interpretation of cataclasites and faults observed in core from Hole
734 BT1B are discussed in detail by Menzel et al. (2020).

735

736 *4.7 Geochemical data*

737

738 The bulk composition of core samples was measured in five different ways: (1) Major and minor
739 element compositions of nine samples were measured by XRF at St. Andrews University. (2) Major
740 and minor element compositions of 74 samples, including those previously analyzed at St. Andrews,
741 were measured via XRF (both fusion and pressed pellets) onboard the Drilling Vessel Chikyu. (3)
742 Major element compositions of the cut face of selected core sections were analyzed onboard using an
743 XRF core scanner. (4) Trace element compositions of a few samples were analyzed onboard via ICP-
744 MS. (5) Trace element compositions of 61 samples were analyzed via ICP-MS at the Université de
745 Montpellier. These data, and subsequent analyses, are tabulated and described in Kelemen et al.
746 (2020b) and Godard et al. (2021), so for brevity we simply refer readers to those other publications.

747

748 **5. Discussion**

749

750 **5.1 Subduction zone setting of listvenite formation**

751

752 On the basis of their structural observations west and northwest of the MoD Mountain area, and U/Pb
753 formation or cooling ages from cross-cutting calcite veins, (60 ± 16 and 58 ± 6 Ma) Scharf et al.
754 (2020) infer that listvenites in the Fanjah area postdate ophiolite emplacement, echoing the qualitative
755 ideas of Stanger (1985) and Wilde et al. (2002). As noted in Sections 2.5 and 4.2, our

756 geochronological and field observations are inconsistent with this interpretation. The listvenite mineral
757 isochron age of 97 ± 29 Ma (2σ) (Falk & Kelemen 2015) yields a 93% chance (1.5σ) that the
758 listvenites formed before 75 Ma, while subduction beneath the ophiolite was still active, and a 97%
759 chance that the listvenites formed before 68 Ma. Thus, the isochron data support listvenite formation
760 during subduction, and show that the calcite veins cutting listvenite, dated by Scharf et al., postdate
761 listvenite formation.

762

763 In this paper, our mapping and structural observations indicate an intact tectonic “stratigraphy” around
764 the basal thrust of the ophiolite, encompassing the allocthanous Hawasina metasediments, overlain
765 by the metamorphic sole, in turn overlain by Banded Unit dunites and harzburgites of the Samail
766 ophiolite mantle section, with essentially horizontal lithologic contacts extending for kilometers. This is
767 the stratigraphy created during subduction beneath the ophiolite, and – together with the isochron – it
768 indicates that these units were juxtaposed during low angle thrusting along the subduction zone. In
769 turn, all the listvenites in the MoD Mountain area are less than a kilometer away from the basal thrust,
770 and have contacts with surrounding mantle peridotites and the metamorphic sole that are parallel to
771 the basal thrust. All these data, taken together, indicate that the listvenites formed along and above
772 the basal thrust of the ophiolite during subduction.

773

774 5.2 Faulting, deformation and veining after listvenite formation

775

776 (U,Th)/He cooling ages (Section 4.3) indicate that the region around MoD Mountain remained above
777 the closure temperature for He diffusion in zircon, $\sim 180^\circ\text{C}$ (Reiners et al 2004), or were reheated
778 above this temperature, during 30 to 60 million years after formation of the igneous crust in the
779 ophiolite and peak metamorphism of the sole. Based on textural observations, it is clear that the
780 breccias and cataclasites sampled in BT1B drill core postdate listvenite formation (Menzel et al 2020).
781 Some may postdate ophiolite emplacement, and may be broadly related to Paleocene to Miocene
782 uplift and extension during formation of the nearby Jebel Akdar and Saih Hatat domes. On the other
783 hand, some could be related to deformation during subduction beneath the ophiolite. The long term
784 persistence of temperatures above 180°C in this region renders it difficult to distinguish formation from
785 cooling ages using (U,Th)/He data.

786

787

787 5.3 Temperature of listvenite formation

788

789 The temperatures of listvenite formation have been previously constrained using metamorphic phase
790 equilibria, conventional oxygen isotope thermometry, and clumped isotope analyses. Falk & Kelemen
791 (2015) noted the presence of intergrown antigorite (serpentine) + quartz. in the reaction zone between
792 listvenite and serpentinite on the west ridge of MoD Mountain (Figure 2). In some cases, these
793 samples also contain talc. They used Thermocalc (Powell et al 1998), with thermodynamic data from
794 Holland and Powell (2003, 1998), and similar methods using the thermodynamic data of Gottschalk
795 (1997), to estimate that equilibrium coexistence of antigorite, quartz and talc occurs at 80 to 120°C ,

796 depending on the choice and uncertainty of thermodynamic parameters for the minerals, and the
797 (poorly known) pressure at which these assemblages crystallized. For this paper, we obtained similar
798 using Perple_X (<https://www.perplex.ethz.ch/>) (Connolly 1990, Connolly 2005, Connolly 2009) and
799 mineral properties from Holland and Powell.

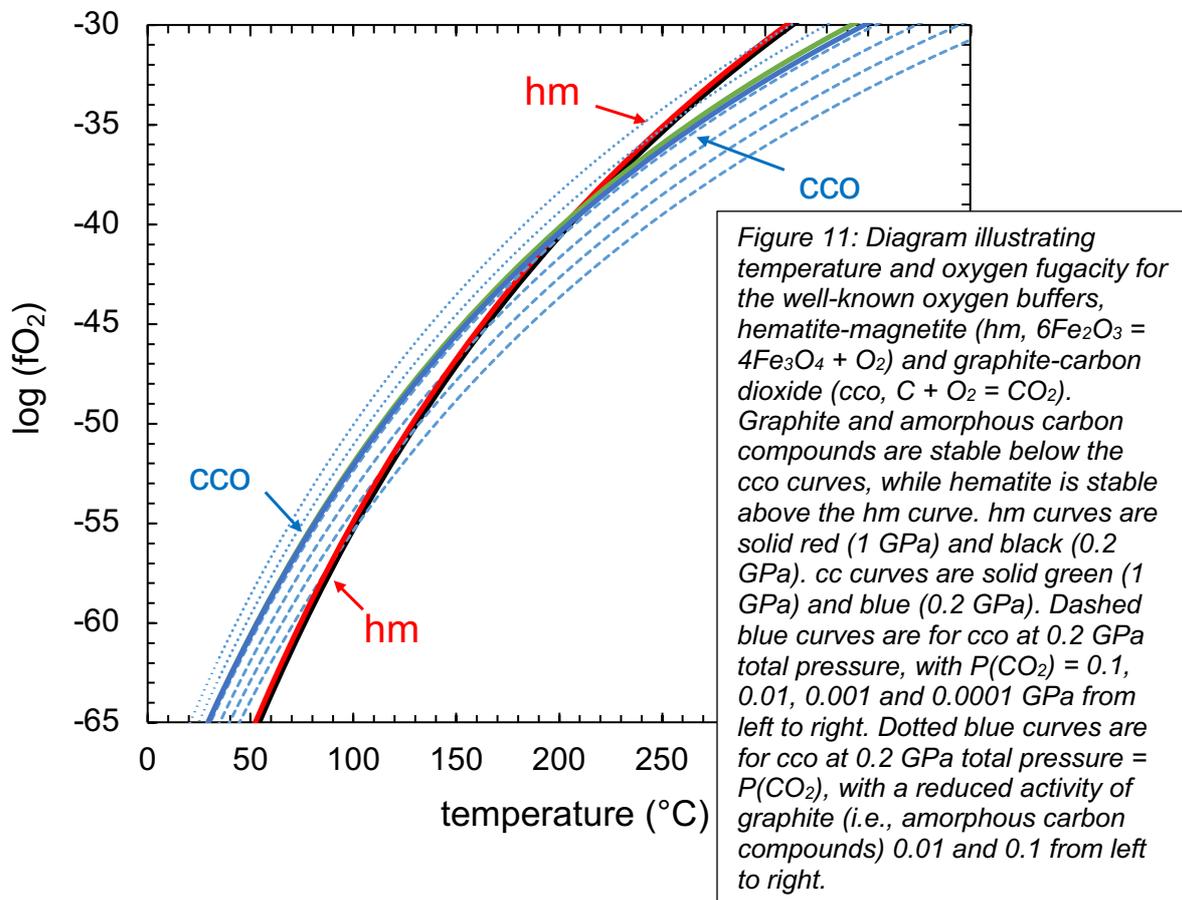
800

801 In contrast, calculations using the Deep Earth Water (DEW) model (Huang & Sverjensky 2019,
802 Sverjensky et al 2014) and the extended Helgeson-Kirkham-Flowers (HKF) aqueous equation of state
803 (Shock et al 1992, Shock et al 1997) do not predict equilibrium coexistence of antigorite + quartz
804 above 15°C. Since antigorite-quartz intergrowths indicate coeval crystallization of both phases, in
805 rocks that formed at > 80°C, we presume that these latter results stem from incorrect extrapolation of
806 thermodynamic data to low temperature.

807

808 Leaving the DEW results aside, the other temperature estimates based on co-existing antigorite +
809 quartz are broadly consistent with temperature estimates based on $\delta^{18}\text{O}$ in quartz and carbonate
810 minerals in the listvenite, assuming that fluid $\delta^{18}\text{O}$ was similar to seawater, and with clumped isotope
811 analyses of magnesite and dolomite yielding temperatures of 80 to 130°C for listvenite samples (Falk
812 & Kelemen 2015). Observation of quartz spherulites in listvenite, possibly reflecting devitrification of
813 opal, also suggests that listvenite formation occurred in this “low temperature” regime, at ~ 150°C or
814 less, in the presence of aqueous fluid.

815



816

817

818

819 Here we show that veins of intergrown amorphous carbon compounds and hematite sampled in the
820 core also must have formed below $\sim 200^{\circ}\text{C}$ (Figure 11). The observation of “reduced” hydrocarbon
821 species intergrown with oxidized iron minerals in veins may seem surprising at first, but they are
822 mutually stable at low temperature due to the stronger temperature dependence of the iron oxidation
823 state, compared to the carbon oxidation state. Above $\sim 200^{\circ}\text{C}$, reduced, organic carbon compounds
824 and oxidized iron minerals such as hematite cannot coexist at the same oxygen fugacity, but they can
825 crystallize together at moderate oxygen fugacities below $\sim 200^{\circ}\text{C}$. We’ve found that this result is
826 robust across all available sets of internally consistent thermodynamic data, and in the pressure range
827 from 0.2 to 1.0 GPa.

828

829 Fourteen more recent clumped isotope analyses for listvenites and carbonate-bearing serpentinites
830 from BT1B core yield an average temperature of $147\pm 58^{\circ}\text{C}$ (1σ). Ten of the 14 temperature estimates
831 lie within the 1σ range, whereas two are lower (45 ± 5 and $52\pm 8^{\circ}\text{C}$) and the two least precise estimates
832 are higher (227 ± 52 and $247\pm 52^{\circ}\text{C}$) (Beinlich et al 2020). Though a few MoD Mtn listvenites might
833 have formed at temperatures greater than 200°C , such temperatures are too high for crystallization of
834 intergrown amorphous carbon + hematite, they are too high for crystallization of intergrown antigorite
835 + quartz, and they are too high for crystallization of opal. Also, carbonation of peridotite above $\sim 150^{\circ}\text{C}$
836 would form abundant talc + magnesite, whereas talc is absent in most MoD Mountain listvenites, and
837 rare in serpentinite-listvenite contact zones that are gradational over a few meters (Falk & Kelemen
838 2015, Kelemen et al 2020b).

839

840 The range in temperature estimates based on phase equilibrium and clumped isotope ratios from the
841 MoD Mountain listvenites may indicate that mineral assemblages in the listvenites and surrounding
842 serpentinites formed gradually over a range of times and temperatures. In addition, some of the
843 clumped isotope data may record closure temperatures during cooling, rather than the peak
844 temperature at which the MoD Mountain listvenites first crystallized, as proposed for clumped isotope
845 data from fine-grained 10-meter scale magnesite veins in California (Garcia del Real et al 2016).
846 Alternatively, since the highest clumped isotope temperatures from Beinlich et al. are also the most
847 imprecise estimates, perhaps they result from analytical uncertainties or disequilibrium effects. When
848 the 14 clumped isotope temperatures from Beinlich et al. are combined with the 31 older clumped
849 isotope temperatures from Falk and Kelemen, the full data set yields an average of $100 \pm 46^{\circ}\text{C}$ (1σ),
850 with the highest temperatures from Beinlich et al. falling outside the 2.5σ (99% probability) range.

851

852

5.4 Depth of listvenite formation

853

854 The depth of listvenite formation is difficult to constrain. As noted in Section 2.4, published work on
855 the metamorphic sole beneath the Samail ophiolite reports peak temperatures up to 700 to 900°C at
856 pressures ranging from 200 to 1400 MPa, indicative of anomalously hot subduction zone conditions.
857 Common peak pressure estimates, ~ 1200 MPa, indicate depths exceeding the structural thickness of

858 the ophiolite. Thus, either (1) the published range of pressure estimates for the metamorphic sole is
859 the result of uncertainty rather than true variation in depth, and/or (2) the lower few km of the ophiolite
860 mantle section has undergone thinning in some places, and/or (3) the lenses of the metamorphic sole
861 recording the highest pressures migrated upward with respect to the overlying peridotite, and/or (4)
862 some mineral equilibria record tectonic overpressures rather than lithostatic loads. Also, we infer from
863 Sr isotope data that the fluids that formed the listvenites were not derived from the metamorphic sole
864 (Section 5.6, below, and de Obeso et al 2021a). For all these reasons, it is unclear whether the
865 metamorphic pressures inferred for the sole constrain the depth of listvenite formation. However,
866 temperatures and pressures recorded by the sole do provide a window into the thermal evolution of
867 subduction beneath the ophiolite before and during listvenite formation.

868
869 Initiation of subduction, during formation of the metamorphic sole, involved thrusting of a hot mantle
870 wedge over newly formed, hot basaltic crust. Over time, subduction of progressively older oceanic
871 crust and – eventually – the pelagic sediments of the Hawasina Formation would have caused cooling
872 of the subduction zone as it evolved toward a steady state geotherm. A few clumped isotope analyses
873 on calcite in sediments beneath the ophiolite and the metamorphic sole on MoD Mountain yield
874 temperatures of 150 to 200°C (Falk & Kelemen 2015). It is possible that these were peak
875 temperatures during diagenesis of the sediments along a late, steady state subduction geotherm at
876 the pressure and depth recorded by the metamorphic sole in core from Hole BT1B, 800 -1200 MPa,
877 or about 25 to 40 km.

878
879 In turn, even lower temperatures for most listvenite samples may record continued, isobaric cooling of
880 rocks flanking the subduction zone. Temperatures of 100 to 200°C at depths of 25 to 40 km are
881 inferred for fore-arc regions above subduction zones from heat flow data (reviewed in Peacock 1996)
882 predicted for steady state, oceanic subduction geotherms in numerical models (e.g., Peacock 1996,
883 Peacock et al 2005, Syracuse et al 2010), including those recently modeled by Van Keken et al.
884 (2019), and lie within the cold end of the range of PT conditions recorded by subduction-related
885 metamorphic rocks (Hacker 1996, Hacker 2006, Penniston-Dorland et al 2015). Such low
886 temperatures at 25 to 40 km are rare or absent in other tectonic environments.

887
888 To summarize, it is possible that the sediments and the overlying mantle peridotites at the base of the
889 ophiolite were juxtaposed by subduction at the leading edge of the mantle wedge, at a depth of 25 to
890 40 km, and that the MoD Mountain listvenites formed at these depths along a cold, steady state
891 subduction geotherm. Alternatively, if the metamorphic sole has migrated updip with respect to the
892 overlying peridotites, then the listvenites could have formed at lower pressures and shallower depths.

893

894 *5.5 Composition of listvenite protolith and geochemical fluid additions*

895

896 Given the abundance and variety of mineralogically simple veins, many of which are monomineralic,
897 there is substantial compositional variation in listvenites at the millimeter to meter scale. This

898 variability extends to larger scales in some parts of the core. Nevertheless, remarkably enough,
899 average MgO/SiO₂/FeO* (all Fe as FeO) ratios in the listvenites are very similar to those in average
900 residual peridotites from the ophiolite (Figure 12), as discussed further by Okazaki et al. (Okazaki et al
901 2021). These oxides comprise more than 90% of the volatile-free bulk composition of the rock. These
902 data suggest that there was little dissolution and export of major elements from the rocks during
903 transformation of peridotite to serpentinite and then to listvenite as discussed further in Section 5.9.

904

905 On the other hand, serpentinites and listvenites record addition of tens of weight percent H₂O and
906 CO₂ to the original bulk composition of mantle peridotite protoliths. In addition to CO₂, dolomite
907 listvenites clearly record substantial addition of CaO, and – since CaO and Sr concentrations are
908 strongly correlated – of Sr as well.

909

910 Although the shipboard data do not reveal systematic variation in the abundance of magnesite vs
911 dolomite listvenites downhole, there is a clear change in the abundance of both Al and K, together
912 with many other highly incompatible trace elements. Concentrations of these elements are relatively
913 low above the serpentinite band at 80-100 m depth, and much higher below that band (Godard et al
914 2021, Kelemen et al 2020b).

915

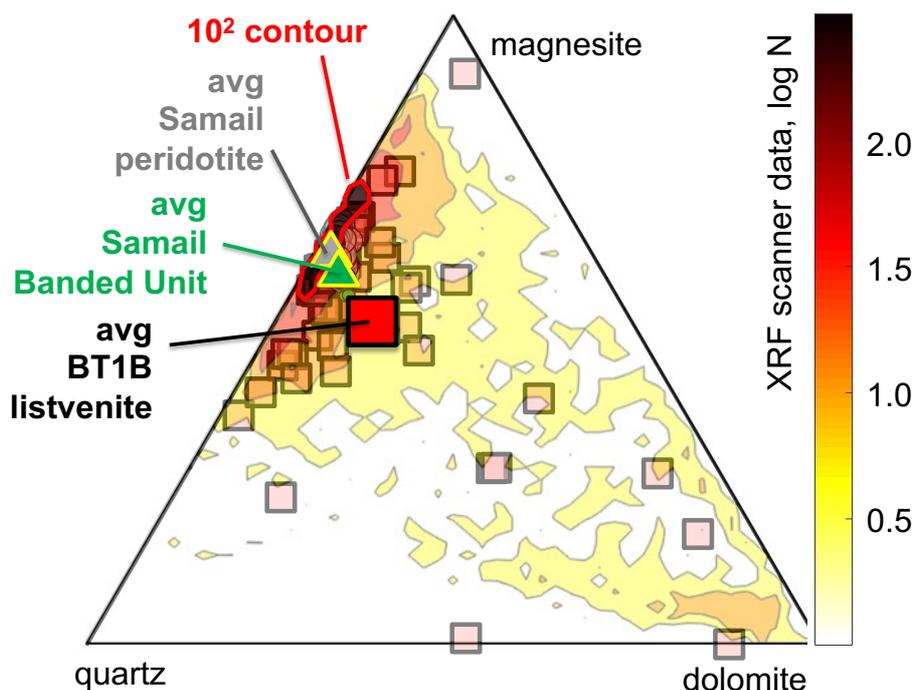
916 Understanding the source for enrichment in these elements is complicated by uncertainty about their
917 concentration in the peridotite protolith. As noted in Sections 2.3, 2.5 and 4.4, a “Banded Unit” of
918 alternating dunite, harzburgite and lherzolite characterizes the base of the ophiolite mantle section in
919 many regions. Some Banded Unit peridotites record high temperature geochemical “refertilization” by
920 reaction of residual mantle peridotites with infiltrating melt or fluid at > 800°C, with addition of calcic
921 pyroxene and Mg-rich hornblende. This produced enrichment in CaO and Al₂O₃ to levels well above
922 those in typical residual mantle peridotites in the Samail ophiolite (Godard et al 2000, Hanghoj et al
923 2010, Monnier et al 2006). Indeed, four out of six harzburgite samples from the Banded Unit on MoD
924 Mountain have Ca and Al contents outside the 1σ range of variability in residual mantle peridotite in
925 the ophiolite (Falk & Kelemen 2015, Godard et al 2021, Kelemen et al 2020c).

926

927 The listvenites below 100 meters depth in core from Hole BT1B have trace element ratios that are
928 distinct from typical peridotites, but characteristic of the Banded Unit (Figure 12 and Godard et al
929 2021), as shown in Figure 13. In particular, middle to heavy rare earth element ratios in the Banded
930 Unit, and in the listvenites, are high compared to typical Samail peridotites. Such enrichment in middle
931 rare earth elements is commonly associated with the presence of igneous hornblende in peridotites.
932 Thus, the listvenites probably inherited these characteristics from the enriched, Banded Unit protolith.

933

934 On the other hand, it is clear that most listvenites have higher Sr concentrations than typical Samail
935 ophiolite peridotites *and* the Banded Unit (de Obeso et al 2021a). Instead, Sr and Ca were added
936 during low temperature alteration, along with H₂O and CO₂. These topics are discussed further by
937 Godard et al. (2021).



938
 939 *Figure 12: Ternary diagram illustrating volume proportions of quartz, magnesite and dolomite,*
 940 *projected from hematite, calculated from whole rock compositions, for Samail mantle peridotites*
 941 *(average in grey triangle, data as large, grey open circles, barely visible beneath the averages and*
 942 *the 10² contour area, Godard et al. 2000; Monnier et al. 2006; Hanghoj et al. 2010}, Banded Unit*
 943 *peridotites near the base of the Samail ophiolite mantle section (small, green open circles, barely*
 944 *visible, Falk & Kelemen 2015, Khedr et al 2013, Khedr et al 2014, Takazawa et al 2003), and*
 945 *listvenites from Hole BT1B and MoD Mtn (open squares, Falk & Kelemen 2015, Kelemen et al*
 946 *2020b), superimposed on contoured histogram of mineral proportions from shipboard XRF scanner*
 947 *data. Contour interval 10². Okazaki et al. (2021) provide more thorough interpretation of shipboard*
 948 *XRF scanner data plus X-Ray Computed Tomography data on the whole core. Average listvenite,*
 949 *Banded Unit and Samail mantle peridotite compositions are provided in Supplementary Table 2.*

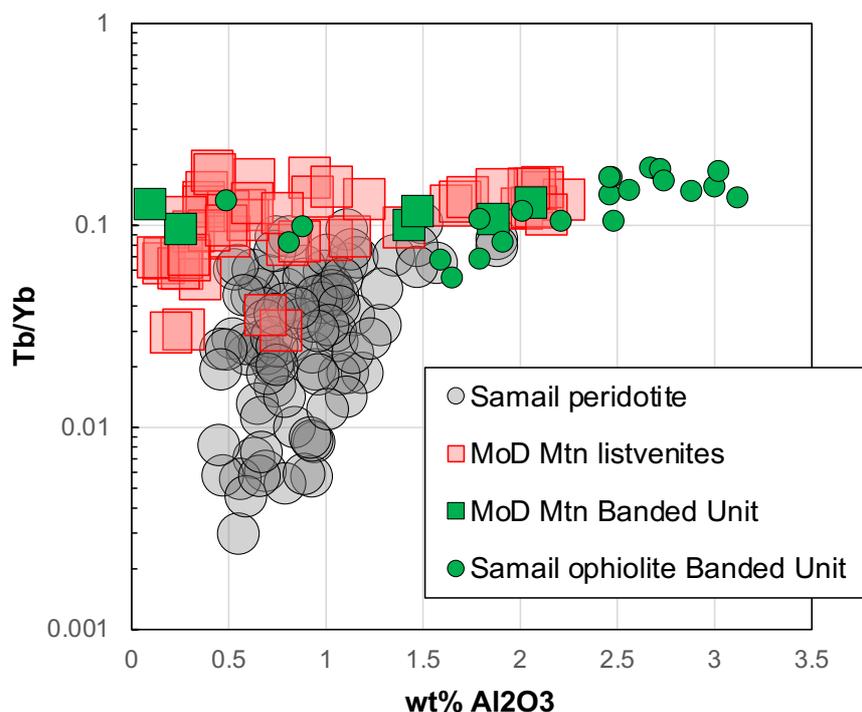


Figure 13: Wt% Al₂O₃ versus Tb/Yb ratios in bulk rock compositions of MoD Mtn listvenites (open squares, Falk & Kelemen 2015, Godard et al 2021, Kelemen et al 2020b), and MoD Mountain peridotites that host listvenites (green squares, Falk & Kelemen 2015, Godard et al 2021), compared to typical Samail mantle peridotites (grey open circles, Godard et al 2000, Hanghoj et al 2010, Monnier et al 2006), and Banded Unit peridotites from the base of the ophiolite (Khedr et al 2013, Khedr et al 2014, Takazawa et al 2003).

5.6 Source of fluid for listvenite formation

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Present day Sr isotope ratios in listvenites and serpentinites from MoD Mtn range from ~ 0.708 to 0.715 (de Obeso et al 2021a, Falk & Kelemen 2015). Using current Rb/Sr contents in these samples, age corrected $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at 96 Ma range from ~ 0.708 to 0.714, much higher than the range of Sr ratios in Samail ophiolite peridotites (0.703 to 0.707, Benoit et al 1999, Gerbert-Gaillard 2002, Gregory & Taylor Jr 1981, Lanphere et al 1981, McCulloch et al 1980, McCulloch et al 1981), the range in Late Cretaceous to modern seawater (~ 0.7075 to 0.7081), or the range in peridotite-hosted ground water in the Samail ophiolite (~0.7065 to 0.7092, Weyhenmeyer 2000). Thus, the Sr-, Ca- and CO₂-rich fluid(s) that modified the mantle overlying the basal thrust of the ophiolite had relatively high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios compared to fresh, residual mantle peridotites.

Initially, we expected that the metamorphic sole, as sampled by core from Hole BT1B, might be the source of fluids that formed listvenites in overlying peridotites, or at least might be analogous to the source of these fluids. However, this is not consistent with the Sr isotope data on the sole in core from Hole BT1B. Measured and age-corrected Sr isotope ratios in the metamorphic sole are consistently lower than corresponding ratios in the listvenites (de Obeso et al 2021a).

Instead, pelagic, clastic units of the underlying Hawasina sedimentary rocks have measured and age-corrected Sr isotope ratios that span the same range as those in the listvenites (de Obeso et al 2021a). Thus, these sedimentary units in the Hawasina may be analogous to subducted sedimentary rocks that produced CO₂-bearing fluids which, in turn, formed the MoD Mountain listvenites. This is likely, despite the presence of C- and Sr-rich limestone and dolomite units with lower Sr isotope ratios in the Hawasina Formation, because devolatilization of clay and mica bearing, clastic metasediments produces abundant, CO₂-rich aqueous fluids, while limestone and marble remain relatively refractory at low to moderate temperature, subduction zone conditions (e.g., Kerrick & Connolly 2001, Stewart & Ague 2020).

Indeed, there is evidence for a deeply subducted component with terrigenous isotope characteristics – like those of the Hawasina clastic sedimentary rocks – elsewhere in the Samail ophiolite. A series of felsic intrusions in the sole, mantle and lower crust along the length of the ophiolite have low, age-corrected $^{143}\text{Nd}/^{144}\text{Nd}$ (and thus, presumably, high $^{87}\text{Sr}/^{86}\text{Sr}(t)$), attributed to melting of high-grade metasediment in the subduction zone below the ophiolite (Amri et al 2007, Briquet et al 1991, Cox et al 1999, Haase et al 2016, Haase et al 2015, Lippard et al 1986, Rioux et al 2021a, Rioux et al 2013, Rioux et al 2021b, Rollinson 2015, Spencer et al 2017).

A complication is that the clastic units in the Hawasina formation have $\delta^{13}\text{C}$ less than -4 per mil, whereas listvenites have $\delta^{13}\text{C} > -3$ per mil. These differences in carbon isotope ratios can be understood as the result of temperature dependent carbon isotope fractionation. As discussed in more detail in de Obeso et al. (2021a), at temperatures greater than ~ 300°C, dissolved CO₂ in

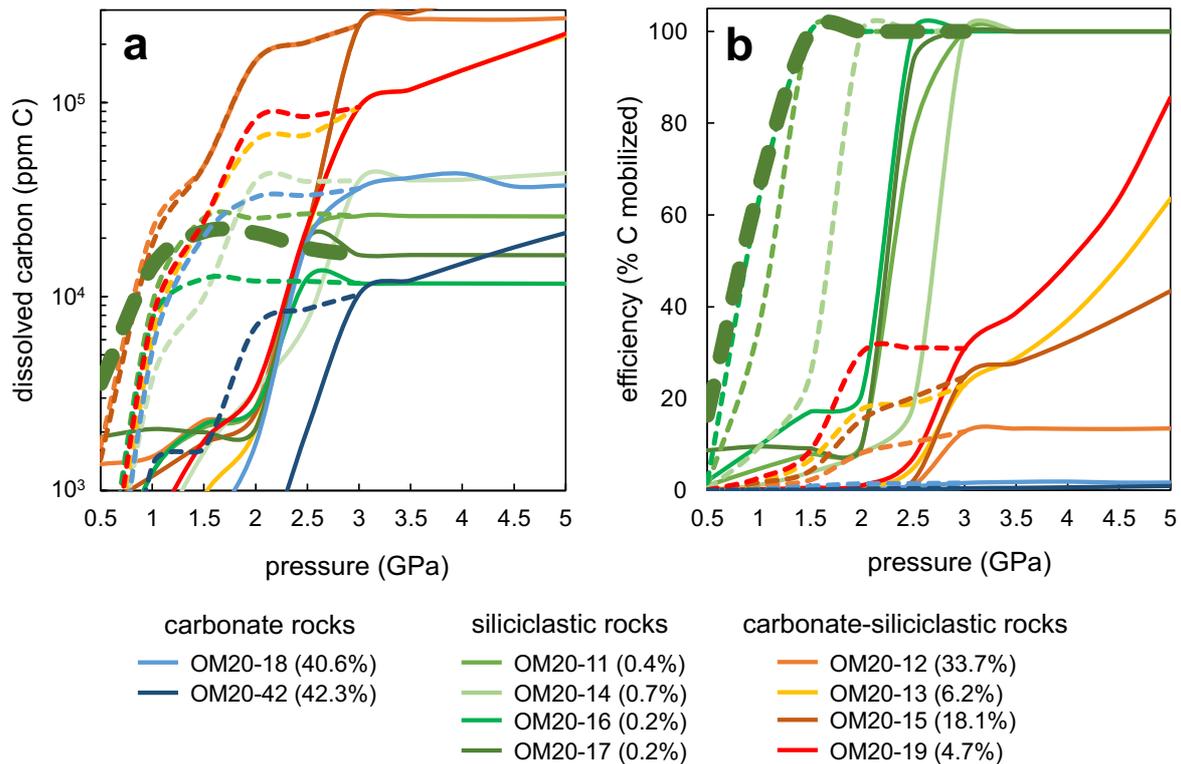
991 aqueous fluids has $\delta^{13}\text{C}$ higher than co-existing calcite and dolomite (Deines 2002, Horita 2014). At
992 lower temperatures, calcite and dolomite have $\delta^{13}\text{C}$ higher than co-existing fluids. Dolomite and
993 magnesite crystallized at relatively low temperature, from aqueous fluids that acquired their carbon
994 isotope ratios during higher temperature devolatilization of Hawasina clastic sediment compositions,
995 would have $\delta^{13}\text{C}$ in the range of 1.0 to -3.0‰, as observed in the MoD Mountain listvenites. In
996 addition, low carbon solubilities in low temperature, low pressure aqueous fluids saturated in
997 carbonate minerals in mineral assemblages similar to those in the Hawasina clastic sedimentary
998 rocks (Figure 22 and associated text in Chapter 4, Falk 2014, Kelemen & Manning 2015) may be
999 insufficient to produce the MoD Mountain listvenites (Falk & Kelemen 2015)de Obeso, 2021 #300}.

1000

1001 Based on the data and reasoning described in the previous paragraph, we hypothesize that
1002 subduction zone devolatilization at 400 to 600°C produced CO₂-rich aqueous fluids that then cooled
1003 and decompressed by flow up the subduction zone, and reacted with peridotite at less than 200°C to
1004 produce the MoD Mountain listvenites. To quantify this hypothesis, we made thermodynamic
1005 calculations with the compositions of solid reactants given in **Supplementary Table 2**, methods
1006 described in **Section 3**, and results outlined in **Figures 14 and 15**. As the source of fluid, we chose
1007 sample OM20-17, a pelitic end-member from among the Hawasina clastic sedimentary rocks
1008 analyzed by Falk & Kelemen (2015) and de Obeso et al. (2021a). As the peridotite reactant, we used
1009 an average Samail harzburgite composition calculated from published studies (Godard et al 2000,
1010 Hanghoj et al 2010, Monnier et al 2006).

1011

1012 Devolatilization of clastic Hawasina sediments, including OM20-17, is predicted to produce fluids with
1013 ~ 20,000 ppm dissolved C at ~ 400°C to ~ 600°C along subduction zone geotherms (Figure 14).
1014 Closed system decompression and cooling of fluid produced from OM20-17 to 100 to 300°C, and 0.5
1015 to 1 GPa produced no significant change in the composition of this modeled fluid. (Modeling open
1016 system, reactive transport of this fluid, updip along a subduction zone geotherm, is beyond the scope
1017 of this paper, as is modeling the fate of subduction zone fluids that have more than 10 wt% CO₂ –
1018 predicted for mixed siliciclastic-carbonate rocks (Figure 14) – as they cool and decompress).



1019
 1020 *Figure 14: Calculated dissolved carbon concentrations at a water/rock ratio of 5% (a) and extent of*
 1021 *carbon removal (b) for samples of Hawasina sediments in the MoD Mountain area (Supplementary*
 1022 *Table 2 in de Obeso et al 2021a), evolving along cold (550°C at 2.5 GPa) and hot (500°C at 1.5 GPa)*
 1023 *subduction geotherms. Solid curves are results for the average (“cold”) subduction zone geotherm*
 1024 *from Syracuse et al. (2010). Dashed curves follow a hot geotherm suggested by Penniston-Dorland*
 1025 *et al. (2015). The initial carbon contents of the rocks (wt%, all carbon as CO₂) are given in the legend.*
 1026

1027 5.7 Listvenite formation

1028
 1029 Reaction of the model fluid from OM20-17 with peridotite at 100-300°C and 0.5 to 1.0 GPa is
 1030 predicted to produce mineral assemblages similar to those modeled by Klein and Garrido (2011): (1)
 1031 Small masses of “birbirite” (silicified peridotite) at high water/rock ratios and/or low temperatures,
 1032 through (2) moderate masses of listvenite and soapstone (talc-carbonate rocks) at moderate
 1033 water/rock and temperature, to (3) relatively large masses of carbonate-bearing serpentinite at low
 1034 water/rock ratios and/or high temperature (Figure 15). Predicted magnesite and quartz proportions
 1035 correspond closely to observed proportions in MoD Mtn listvenites (Figure 12). Most of the PT
 1036 conditions we modeled produced small amounts of hematite coexisting with magnesite and quartz, as
 1037 observed. Predicted magnesite and siderite proportions correspond to a solid solution with ~ 8 wt%
 1038 FeO, which is a few wt% higher than observed in MoD Mtn listvenites. Most modeled conditions
 1039 produced dolomite in listvenite assemblages at water/rock ratios at water/rock ratios less than 10 (log
 1040 water/rock = 1), consistent with the presence of relatively late, cross-cutting dolomite-bearing veins in
 1041 the listvenites. Most model runs produce small amounts of kaolinite, and very limited proportions of
 1042 muscovite, in listvenite mineral assemblages, consistent with the widespread presence of minor
 1043 amounts of chromian white mica in MoD Mtn listvenites, and in listvenites worldwide. It is possible that
 1044 addition of a thermodynamic model for fuchsite would yield stable white mica, rather than kaolinite,

1045 over a wider range of temperature and water/rock ratios. Alternatively, perhaps some of the green
1046 sheet silicates in listvenites are chrome-bearing clays rather than true micas.

1047

1048 Thus, thermodynamic modeling suggests that the CO₂-bearing aqueous fluids that formed the MoD
1049 Mountain listvenites formed by metamorphic devolatilization in a subduction zone at > 400°C. These
1050 fluids then migrated updip to react with peridotite at the leading edge of the mantle wedge, probably at
1051 a depth less than 40 km. However, this is just a forward model, and there may be other possibilities.

1052

1053 Subhorizontal lenses of listvenite at MoD Mountain contain a cumulative mass of about 2 billion tons
1054 of CO₂ over a strike length of 2 km NS, and 5 km EW, corresponding to 1 million to 400,000 tons of
1055 CO₂ per m along strike. The allochthonous sedimentary units below the ophiolite are about 3 km thick.
1056 Within these, clastic units comprise at least half the section, and contain about 2300 ppm C, or 0.84
1057 wt% CO₂ on average (de Obeso et al 2021a), yielding a total of about 35 tons CO₂ per m along strike,
1058 per m subducted. (As noted above, rocks composed mainly of calcite and/or dolomite in the
1059 subducting sedimentary section would be unlikely to contribute significant amounts of CO₂ to
1060 subduction fluids at temperatures less than 800°C). At subduction velocities of 0.05 to 0.1 m/year,
1061 90% decarbonation of the clastic units in the Hawasina Formations with a density of 2.75 tons/m³, at ~
1062 400-500°C would produce at least 1.7 to 3.5 tons of CO₂ per year per m of strike length. If most of this
1063 CO₂ reacted with peridotite at the depth and temperature of MoD Mtn listvenite formation, this could
1064 supply the observed mass of CO₂ at MoD Mountain in less than 600,000 years.

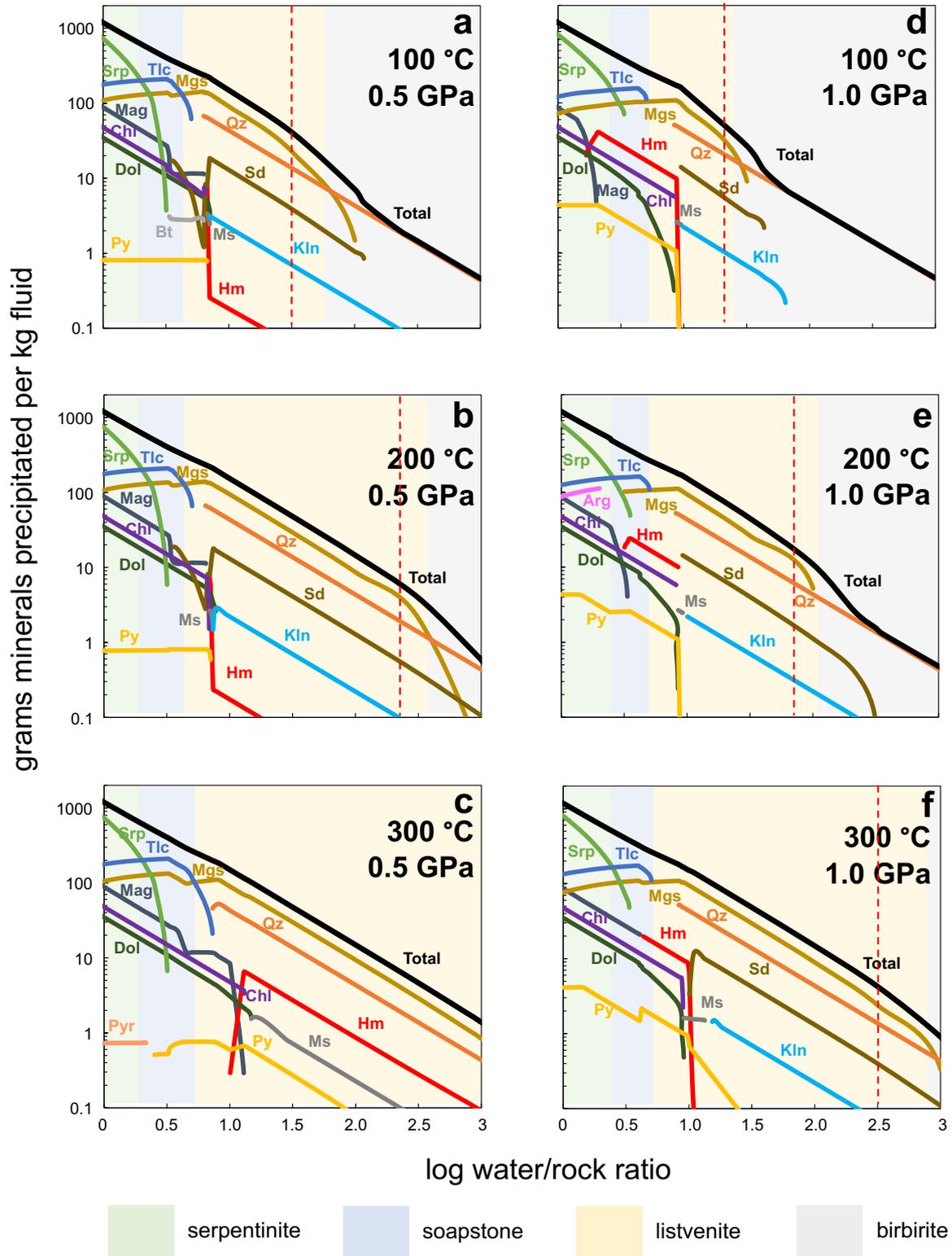
1065

1066 Most of the model results at different conditions predict precipitation of a few weight percent
1067 magnesite (and some dolomite) in the serpentinization domain. This is consistent with observation of
1068 carbonate veins in serpentinites from Hole BT1B, and with the hypothesis that formation of carbonate
1069 veins in the serpentinite zone preceded transformation of the serpentinite host rocks to listvenite (also
1070 see [Figure 6](#) and associated text in [Section 4.4](#),

1071

1072 The fluid temperatures, compositions and fluxes used in these calculations are different from the
1073 constraints used in some calculations by Falk & Kelemen (2015). In that previous work, we explored
1074 the possibility that CO₂ to form the listvenites was supplied over tens of millions of years, carried in
1075 100 to 200°C fluids containing a few hundred ppm dissolved carbon, derived from pore fluids and/or
1076 dewatering of opal and clay minerals, from the Hawasina sedimentary rocks immediately below the
1077 site of listvenite formation at MoD Mountain. However, one of us (Falk!) insisted on mentioning the
1078 possibility that the CO₂ to form listvenites was derived from fluids formed deeper in the subduction
1079 zone, that migrated updip. We now prefer this latter hypothesis, for the reasons outlined above.

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Figure 15: Results of thermodynamic reaction path models of reaction between fluids derived from devolatilization of Hawasina pelitic sedimentary rock sample OM20-17 (Section 5.6) and average Oman harzburgite. Mineral end-member abbreviations Qz quartz, Sd siderite, Mgs magnesite, Klin kaolinite, Ms muscovite, Dol dolomite, Chl chlorite, Py pyrite, Tlc talc, Srp serpentine (chrysotile), Pyr pyrrhotite. Red, vertical dashed line indicates where magnesite/quartz molar and volume proportions are ~ 2:1, as observed in magnesite listvenites from MoD Mtn (e.g., Figure 12).

1089 Updip migration of fluids in a subduction zone has been predicted in some simplified dynamic models
1090 of fluid flow in a viscously deforming subduction zone with high permeability (Wilson et al 2014).
1091 However, the tendency of fluid buoyancy to drive vertical fluid flow may often dominate subduction
1092 zone fluid fluxes. Thus, formation of relatively shallow listvenites, like those at MoD Mountain, may be
1093 localized and unusual. Elsewhere, CO₂-bearing fluids may migrate vertically into overlying mantle
1094 peridotite at greater depth (e.g., Kelemen & Manning 2015). It is interesting to ponder how subduction
1095 zone CO₂ fluxes may be partitioned between these different transport and mineralization processes.

1097 *5.8 Multiple reaction fronts*

1098
1099 The thermodynamic models presented in Sections 5.6 and 5.7 provide a starting point for
1100 understanding “chromatographic effects” during transformation of peridotite to serpentinite. As can be
1101 seen in Figure 15, our reaction path models predict sharp fronts where serpentinite is replaced by
1102 soapstone, and then by listvenite. Talc-bearing, soapstone assemblages are predicted to crystallize in
1103 a limited range of conditions, consistent with the fact that talc is rare in core from Hole BT1B, and in
1104 hand specimens from MoD Mtn, where it is almost entirely restricted to narrow (~ 1 m scale) transition
1105 zones between listvenite and serpentinite. If we were to use different thermodynamic data, talc might
1106 be even less abundant, or absent in models at 100°C, because talc is predicted to be unstable below
1107 ~ 100°C with respect to antigorite + quartz when using mineral data from Holland and Powell or
1108 Gottschalk, together with the Redlich-Kwong equation of state for H₂O- CO₂ fluids as modified by
1109 Kerrick and Jacobs (1981) and by Holland and Powell (2003).

1110
1111 In the model results presented in Figure 15, with reaction progress increasing from high fluid/rock
1112 ratios on the right to low fluid/rock ratios on the left, magnesite + quartz and magnesite + talc become
1113 unstable with respect to serpentine as dissolved carbon in the fluid is exhausted. Because carbon is a
1114 minor constituent of aqueous fluid, but a major component of the listvenite assemblage, exhaustion of
1115 dissolved carbon is predicted to occur at a fluid/rock ratio much greater than 1 (log fluid/rock > 0). Of
1116 course, because aqueous fluid is composed mainly of H₂O, the potential for serpentinization of
1117 peridotite continues to much lower fluid/rock ratios.

1118
1119 Although we cannot model it, we can also predict that – in the presence of pervasive fluid flow on the
1120 grain scale – there could also be a sharp front where serpentine replaces olivine at water/rock ratios
1121 less than one. Thermodynamic calculations for simplified olivine serpentinization by Kelemen et al.
1122 (2020a) indicate that olivine + H₂O would be stable with respect to serpentine at 100°C and a partial
1123 pressure of ~ 10⁻² bars, and at 200°C and P(H₂O) ~ 1 bar. While these conditions cannot be modeled
1124 using EQ3/6, we can anticipate that low partial pressures of H₂O – much lower than lithostatic
1125 pressures – are produced along grain boundaries and near the tips of incipient fractures and veins,
1126 especially where fluid has been almost completely consumed by peridotite hydration reactions. Under
1127 these conditions, there could be a sharp front where serpentine (at higher fluid pressures) becomes
1128 stable relative to olivine (at lower fluid pressure).

1129

1130 Throughout the mantle section of the Samail ophiolite, residual mantle peridotites commonly contain
1131 about 50 to 80% serpentine, as inferred from the fact that bulk rock analyses yield loss on ignition
1132 (mostly, H₂O) of 8 to 10 wt% as compared to 13 to 16 wt% H₂O in completely serpentinized, Mg end-
1133 member harzburgite and dunites. These partially serpentinized peridotites commonly show a “mesh
1134 texture”, with relict olivine and pyroxene “cores” transected by a “mesh” of cross-cutting serpentine
1135 veins – typically 10 to 100 microns apart (Francis 1956, Green 1961, Green 1964, Raleigh & Paterson
1136 1965). In some regions within the Samail ophiolite, particularly areas of relatively subdued topography
1137 that have undergone extensive, penetrative weathering, relict mantle minerals in the mesh cores are
1138 completely replaced by serpentine (e.g., OmanDP Sites BA1, BA2, BA3 and BA4, Kelemen et al
1139 2021, Kelemen et al 2020c). However, along the steep canyons and narrow ridges that are typical of
1140 outcrops in the mantle section of the ophiolite, subject to relatively rapid erosion, the pervasive
1141 presence of the serpentine vein mesh surrounding relict mantle minerals attests to relatively rapid
1142 fluid transport in fractures and veins, compared to slow transport of H₂O into the mesh cores by
1143 diffusion and/or imbibition.

1144

1145 In contrast, as noted above, the serpentinites sampled in core from Hole BT1B contain no relict olivine
1146 or orthopyroxene, though pyroxene pseudomorphs (“bastites”) are evident. A zone of 100%
1147 serpentinized peridotites a few meters thick was sampled by Falk & Kelemen (2015) in a transect
1148 across a listvenite-peridotite contact on the watershed ridge east of the summit MoD Mountain.
1149 Outside this zone, samples of peridotite had compositions and textures typical of partially
1150 serpentinized residual mantle peridotites throughout the ophiolite. Based on these observations, we
1151 infer that there is a 100% serpentinite zone a few meters thick, with sharp fronts – less than a meter
1152 thick, between serpentinite and listvenite on one side, and between partially and completely
1153 serpentinized peridotite on the other side.

1154

1155

5.9 Volume change during listvenite formation

1156

1157 The likely volume change during fluid-rock reactions has long been debated. Whereas Coleman &
1158 Keith (1971) proposed that serpentinization involved simple addition of H₂O to peridotite, with no
1159 significant change in the volatile-free solid composition, Carmichael (1987), Nahon & Merino (1987),
1160 and Fletcher & Merino (2001) argued that such reactions take place at nearly constant volume, with
1161 addition of some components balanced by dissolution and export of others. Fletcher & Merino
1162 provided quantitative calculations to support this hypothesis. Where a fluid that is super-saturated in a
1163 new mineral phase, A, starts to crystallize A within a host mineral B that is initially in equilibrium with
1164 fluid, expansion of B around A leads to an increase in local effective stress. In turn, because chemical
1165 potential is proportional to the mean stress, this reduces supersaturation in A and leads to
1166 undersaturation in B. This process continues, with very small volume changes, until the rate of
1167 crystallization of A becomes equal to the rate of dissolution of B, at a steady state stress.

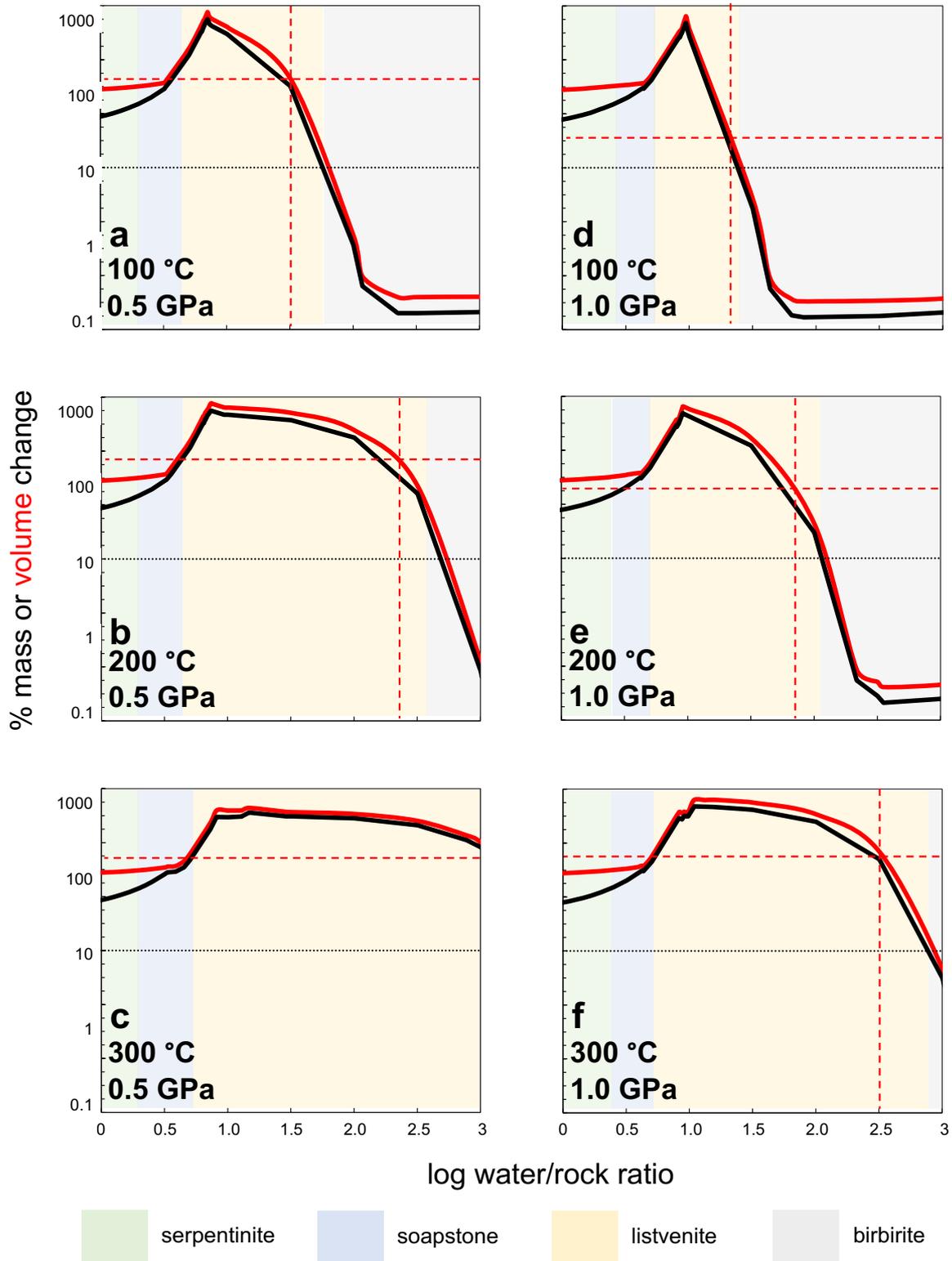
1168

1169 Using the methodology of Fletcher and Merino (2001) and a saturation index of 2 (as they did),
1170 Kelemen and Hirth (2012) calculated that the steady state, effective stress during replacement of
1171 olivine with serpentine is ~ 40 MPa. However, because olivine is very far from equilibrium with water
1172 at low temperature, the saturation index for water reacting with olivine to form serpentine at 50 to
1173 250°C and $P(\text{H}_2\text{O}) > 1$ bar is close to 10^7 , and the steady state, effective stress estimated using the
1174 method of Fletcher and Merino is ~ 800 MPa (Kelemen & Hirth 2012). Clearly, such a large differential
1175 stress cannot be sustained within most rocks, which will deform at a lower stress, before the steady
1176 state can be reached, either via ductile mechanisms (if reactions are slow and temperatures are high)
1177 or via fracture and frictional deformation (if reactions are fast and temperatures are low). The latter
1178 outcome is sometimes termed “reaction-induced cracking” (Jamtveit et al 2009, Rudge et al 2010) or
1179 “reaction-driven cracking” (Kelemen & Hirth 2012). Thus, while some workers still disagree over the
1180 extent of volume change in specific replacement processes, the approach of Fletcher and Merino
1181 nicely explains a continuum between nearly constant volume replacement of one mineral by another
1182 at high temperature, close-to-equilibrium conditions, and large volume changes accommodated by
1183 fractures and frictional sliding at low temperature, far-from-equilibrium conditions.

1184
1185 As noted in [Section 5.5](#), despite dramatic, local variability, the average major element composition of
1186 listvenites from MoD Mountain – in drill core and surface samples – is strikingly similar to the average
1187 composition of residual mantle harzburgites in the Samail ophiolite. Together, the concentrations of
1188 MgO, SiO₂ and FeO* (all Fe as FeO) account for more than 90% of the volatile-free bulk composition
1189 of listvenite samples. Thus, the fact that average Mg/Si/Fe ratios in the listvenites are almost identical
1190 to those in Samail peridotites suggests that either (1) large scale dissolution of the peridotite protoliths
1191 was nearly congruent, exporting dissolved, major elements in approximately their initial proportions, or
1192 (2) there was little dissolution and export of major elements in the protolith during addition of CO₂ to
1193 form listvenites, and addition of H₂O to form serpentinites.

1194
1195 Thermodynamic models, experimental data, and observations of natural rock samples strongly favor
1196 the second of these hypotheses. The solubility of silicate and Fe-oxide minerals in rock-buffered
1197 aqueous fluids at low temperature is too low to allow for large scale dissolution and export of major
1198 elements in open system, fluid-rock reactions. In turn, models of addition of CO₂ and/or H₂O to
1199 peridotites, predict very little removal of other species, together with large increases in the mass and
1200 volume of the solid products of reaction. Birbirite formation may involve net volume and mass loss
1201 due to extensive dissolution of peridotite reactants at water/rock ratios greater than ~ 100. However,
1202 the models of listvenite formation illustrated in [Figure 15](#) yield predicted mass and volume increases
1203 of 10 to 55 percent relative to an anhydrous, peridotite reactant, as illustrated in [Figure 16](#). Similar
1204 results have been produced by thermodynamic models of serpentinitization (volume increase of 40-
1205 60%, de Obeso & Kelemen 2018, Malvoisin 2015), experimental observation of closed system
1206 serpentinitization (30-60%, Klein & Le Roux 2020) and analysis of microstructures in partially
1207 serpentinitized peridotites formed in an open system (59±30 to 74±36%, Malvoisin et al 2020).

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Figure 16: Calculated mass and volume change relative to an anhydrous peridotite, for the reaction path models illustrated in Figure 15. Dashed, vertical red lines indicate where molar and volume proportions of magnesite/quartz reach 2:1, as observed in MoD Mtn listvenites (e.g., Figure 12). Dashed, horizontal line highlights the minimum increase in solid volume calculated for listvenite formation.

1216 These modeled and observed volume changes approximate those resulting from simplified, Fe-free,
 1217 stoichiometric reactions. Thus, hydration of olivine to form serpentine and brucite,
 1218
$$2\text{Mg}_2\text{SiO}_4 + 3\text{H}_2\text{O} = \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Mg}(\text{OH})_2, \quad (1)$$

 1219 and hydration of olivine + orthopyroxene to form serpentine,
 1220
$$\text{Mg}_2\text{SiO}_4 + \text{MgSiO}_3 + 2\text{H}_2\text{O} = \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4, \quad (2)$$

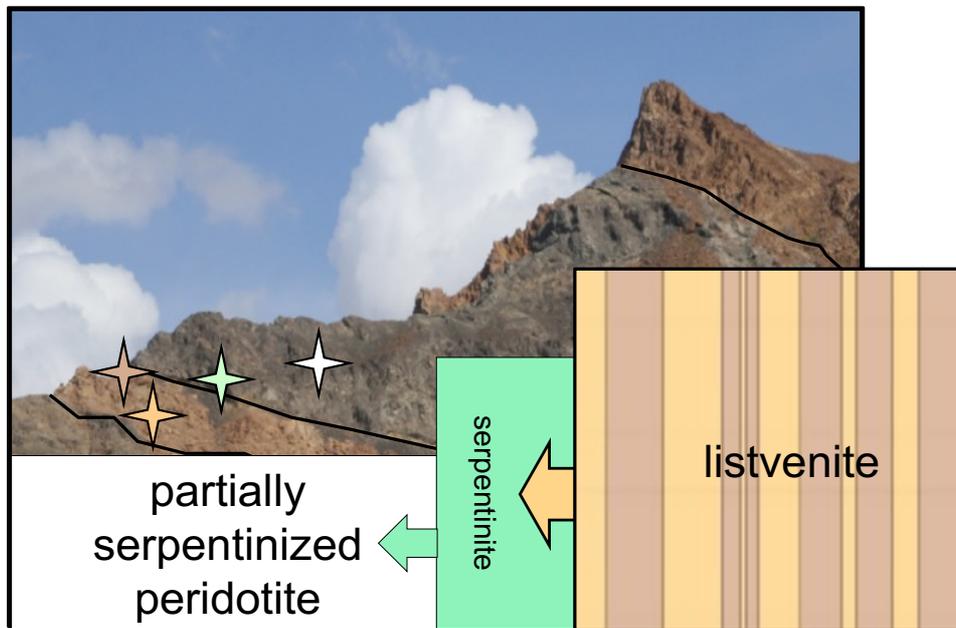
 1221 can produce 52 and 63% increases in the solid volume, respectively. (Volume change calculated as
 1222 100% (product volume -reactant volume)/(reactant volume)). Direct carbonation of olivine
 1223
$$\text{Mg}_2\text{SiO}_4 + 2\text{CO}_2 = 2\text{MgCO}_3 + \text{SiO}_2, \quad (3)$$

 1224 and olivine + orthopyroxene,
 1225
$$\text{Mg}_2\text{SiO}_4 + \text{MgSiO}_3 + 3\text{CO}_2 = 3\text{MgCO}_3 + 2\text{SiO}_2, \quad (4)$$

 1226 can lead to 85% and 74% increases in the solid volume, respectively. And, carbonation of serpentine
 1227 plus brucite
 1228
$$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Mg}(\text{OH})_2 + 4\text{CO}_2 = 4\text{MgCO}_3 + 2\text{SiO}_2 + 3\text{H}_2\text{O}, \quad (5)$$

 1229 and serpentine alone
 1230
$$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 3\text{CO}_2 = 3\text{MgCO}_3 + 2\text{SiO}_2 + 2\text{H}_2\text{O}, \quad (6)$$

 1231 both produce solid volume increases ~ 22%.
 1232



1233
 1234 *Figure 17: Schematic illustration of sequential volume changes during replacement of partially*
 1235 *serpentinized peridotite by serpentinites and then replacement of serpentinites by listvenites. The*
 1236 *height of the rectangles corresponds to the relative volumes, produced by reaction of CO₂-bearing*
 1237 *fluid with an initial, anhydrous peridotite. The tan and brown stripes in the “listvenite” represent*
 1238 *alternations of different listvenite compositional bands. Stars on photo of the SW side of MoD Mtn*
 1239 *illustrate position of listvenite, serpentinite and partially serpentinized peridotite samples (Falk &*
 1240 *Kelemen 2015).*
 1241

1242 Because porosities in peridotite, serpentinite and listvenite rarely if ever exceed 5%, all of these solid
 1243 volume changes must be accommodated mainly by expansion of the entire rock volume. It is
 1244 interesting to speculate how much uplift – and/or lateral expansion – in forearc regions is caused by

1245 hydration and carbonation of the mantle wedge. However, at the plate tectonic scale, the rates of
1246 reactions similar to those outlined in equations (1-6) are unknown. It is likely that the strains due to
1247 reaction are comparable to, or smaller than, other rates of deformation at convergent plate
1248 boundaries, rendering the effect of solid volume expansion difficult to detect at the regional scale.

1249

1250 Based on the considerations outlined in this section, it is likely that large increases in the solid volume
1251 occurred during formation of the MoD Mountain listvenites, and were accommodated mainly by
1252 reaction-driven cracking, frictional sliding along existing fractures, and/or reaction-assisted granular
1253 flow (Menzel et al 2021). The presence of abundant, antitaxial magnesite, magnesite-hematite, and
1254 Fe-oxide veins in both serpentinites and listvenites is qualitatively consistent with a reaction-driven
1255 cracking process. However, we have not identified any obvious strain markers that would allow a
1256 quantitative evaluation of this hypothesis using rock textures.

1257

1258 Building upon an idea from Hansen et al. (2005), the Shipboard Scientific Party developed the
1259 hypothesis that large volume increases due to hydration of olivine and pyroxene (reactions 1 & 2) may
1260 have initially formed fractures at (and beyond) a serpentinization front – not observed in drill core, but
1261 traversed by Falk & Kelemen (2015) – and these fractures were conduits for fluid flow and sites of
1262 localized deformation during the smaller volume changes due to carbonation of serpentinites
1263 (reactions 5 and 6) as schematically illustrated in [Figure 17](#).

1264

1265 *5.10 Low temperature ductile deformation in subduction zones*

1266

1267 As noted above, the listvenites at MoD Mountain may have formed at depths of 25 to 40 km, at
1268 temperatures less 200°C, yielding low temperature “geotherms” of 5 to 8°C/km depth. Such small
1269 increases of temperature with depth are characteristic of the forearc above subduction zones
1270 (Peacock 1996). High fluid pressures at these depths may account for the somewhat surprising
1271 indications of low temperature, ductile deformation in core samples from Hole BT1B, based on the
1272 observed crystallographic preferred orientation (CPO) in quartz, magnesite and serpentine in core
1273 samples ([Section 4.4, Figure 10](#)).

1274

1275 Some of the fabrics illustrated in [Figure 10](#) could be inherited. For example, in early formed,
1276 magnesite-hematite veins, magnesite forms parallel crystals, perpendicular to vein margins, with
1277 small misorientations between adjacent crystals. When these veins are parallel (because they form
1278 that way, or after they are transposed), this imparts a CPO to the sample, and may also give the
1279 impression that sub-grain boundaries are present, even if there was no deformation of magnesite
1280 crystals via dislocation creep. Similarly, quartz replacing opal may inherit a CPO, or a CPO may arise
1281 due to anisotropic stress during recrystallization, without substantial strain.

1282

1283 On the other hand, the serpentine mylonite illustrated in [Figure 10](#) almost certainly records large
1284 strains due to distributed deformation along grain boundaries. Moreover, clear examples of ductile

1285 deformation and shear zones with classical indicators of substantial strain indicate that ductile
1286 deformation was active during the initial stages of listvenite formation, perhaps assisted by positive
1287 feedback between weakening, due to reaction-induced recrystallization, and porosity enhancement
1288 due to deformation, as discussed by Menzel et al. (2021). An important role for ductile deformation in
1289 reaction zones at the top of subducting oceanic crust may help to explain why, in the relatively hot
1290 Cascadia and SW Japan subduction zones, there are very few earthquakes at the top of the
1291 subducting crust (Abers et al 2009, Abers et al 2013, Hirose et al 2008).

1292

1293

6. Conclusions

1294

1295 Observations of drill core of listvenite (completely carbonated peridotite), serpentinite, and
1296 subduction-related metamorphic rocks from OmanDP Hole BT1B provide constraints on temperature,
1297 depth, and deformation during mass transfer of H₂O and CO₂ from subducted sediments into
1298 overlying mantle peridotites at the leading edge of the mantle wedge. Listvenites, and a surrounding
1299 zone of serpentinite, formed at temperatures less than ~ 200°C and poorly constrained depths of 25
1300 to 40 km. Serpentinization and carbonation involved reaction of partially serpentinized, residual
1301 mantle peridotite with CO₂-rich, aqueous fluids produced by devolatilization of subducting, clastic
1302 sediments analogous to the Hawasina formation, probably at 400 to 600°C. These fluids cooled as
1303 they were transported up the subduction zone to the site of listvenite formation.

1304

1305 Such processes could play a significant role in the global carbon cycle. Not all listvenites form above
1306 subduction zones. However, listvenites are found at and near the basal thrust in other ophiolites,
1307 worldwide (Akbulut et al 2006, Borojević Šoštarić et al 2014, Escayola et al 2009, Menzel et al 2018,
1308 Quesnel et al 2016, Quesnel et al 2013, Scarsi et al 2018, Sofiya et al 2017, Ulrich et al 2014). The
1309 leading edge of the mantle wedge – and subduction modified mantle that has later been incorporated
1310 into the continental mantle lithosphere – may be a globally important reservoir for carbon (Foley &
1311 Fischer 2017, Kelemen & Manning 2015, Li et al 2017, Scambelluri et al 2016)

1312

1313 During BT1B listvenite formation, total solid volume increased by tens of percent due to hydration
1314 followed by carbonation. While core and surface samples provide few direct constraints on the
1315 mechanism that accommodated this expansion, one hypothesis is that large volume changes during
1316 hydration of olivine and pyroxene along a serpentinization front caused large stresses and fractures
1317 that accommodated expansion via frictional sliding, and provided secondary porosity for the CO₂-rich
1318 fluids that transformed serpentinites to listvenites.

1319

1320 Based on observed crystallographic preferred orientation in quartz, magnesite and serpentine in
1321 macroscopically identified shear zones, it is inferred that ductile deformation of listvenite and
1322 serpentinite occurred under low temperature conditions at the base of the mantle wedge during
1323 subduction. Low temperature ductile deformation, coeval with serpentinization and listvenite
1324 formation, may have been facilitated by recrystallization associated with the hydration and carbon

1325 mineralization processes, as discussed in more detail by Menzel et al. (Menzel et al 2021). Such a
1326 process could be active in subduction zones where the interface between subducting oceanic crust,
1327 sediments, and hanging wall peridotites is aseismic.

1328

1329

6. Author contributions

1330

1331 Kelemen and de Obeso conducted field mapping at MoD Mountain. de Obeso made new Sr and C
1332 isotopic analyses of listvenites, the metamorphic sole and the underlying sedimentary rocks, updating
1333 work by Falk & Kelemen (2015). Stockli carried out the reconnaissance (U,Th)/He analyses of zircons
1334 from the metamorphic sole and lower crust, using zircon separates samples provided by Rioux.
1335 Godard expertly led the BT1B geochemistry team onboard Drilling Vessel Chikyu, and then heroically
1336 continued with analyses at the Université de Montpellier on behalf of the Shipboard Scientific Party.
1337 Okazaki labored with Kelemen on the triangular histogram of shipboard XRF scanner data. Leong and
1338 de Obeso conducted the EQ3/6 thermodynamic modeling, in consultation with Kelemen. Working with
1339 his computer in 46°C weather on the drill site, Manning provided key insights into conditions for
1340 coexisting hematite and organic carbon compounds. Ellison supervised Kelemen's Raman
1341 spectroscopy analyses at the University of Colorado, Boulder, and offered essential advice and data
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1394 <http://publications.iodp.org/other/Oman/OmanDP.html>, where they are freely available, with more
1395 detailed references provided in the figure captions. [Figures 1, 2, 5, and 7-17, Supplementary Figures](#)
1396 [1 and 2, and Supplementary Tables 1 and 2](#) constitute data that are original with this paper. When
1397 this manuscript is accepted, the tabulated data will be uploaded to the Zenodo repository
1398 (<https://zenodo.org>).

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