1 **Geochemistry and petrology of listvenite in the Samail Ophiolite, Sultanate of**
2 **Oman: Complete carbonation of peridotite during ophiolite emplacement**

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6 **Abstract**

7 Extensive outcrops of listvenite—fully carbonated peridotite, with all Mg in
8 carbonate minerals and all Si in quartz—occur along the basal thrust of the Samail
9 Ophiolite in Oman. These rocks can provide insight into processes including (a) carbon
10 fluxes at the “leading edge of the mantle wedge” in subduction zones and (b) enhanced
11 mineral carbonation of peridotite as a means of carbon storage. Here we examine
12 mineralogical, chemical and isotopic evidence on the temperatures, timing, and fluid
13 compositions involved in the formation of this listvenite. The listvenites are composed
14 primarily of magnesite and/or dolomite + quartz + relict Cr-spinel. In some instances the
15 conversion of peridotite to listvenite is nearly isochemical except for the addition of CO₂,
16 while other samples have also seen significant calcium addition and/or variable, minor
17 addition of K and Mn. Along margins where listvenite bodies are in contact with
18 serpentinized peridotite, talc and antigorite are present in addition to carbonate and
19 quartz. The presence of antigorite + quartz + talc in these samples implies temperatures
20 of 80-130°C. This range of temperature is consistent with dolomite and magnesite
21 clumped isotope thermometry in listvenite (average $T = 90 \pm 15^\circ\text{C}$) and with
22 conventional mineral-water oxygen isotope exchange thermometry (assuming fluid $\delta^{18}\text{O}$
23 near zero). CO₂-bearing fluids responsible for the formation of listvenite were likely
24 derived from underlying calcite-bearing metasediment during emplacement of the
25 ophiolite. An internal Rb-Sr isochron from one listvenite sample yields an age of 97 ± 29
26 Ma, consistent with the timing of emplacement of the ophiolite over allochthonous
27 sediments of the Hawasina group, and autochthonous sediments of the Arabian
28 continental margin. Most of the initial $^{87}\text{Sr}/^{86}\text{Sr}$ values in the listvenite, ranging from

0.7085 to 0.7135, are significantly higher than seawater values and consistent with values measured in the underlying metasediments. While constraints on the pressure of listvenite formation are lacking, the moderate temperatures suggest that listvenites formed at relatively shallow depths in the subduction zone, making release of carbonate-saturated pore-water due to compaction of subducted sediment or low-pressure phase transitions of hydrous minerals, such as clays, probable sources of the CO₂-bearing fluid. Carbonate dissolution from subducted sediments and transfer of CO₂ to the mantle wedge to form listvenites may be an important process in forearc hydrothermal systems. Additionally, the presence of listvenites demonstrate that peridotite carbonation reactions can proceed to completion on large scales, suggesting that *in situ* mineral carbonation of peridotite may offer a viable solution for carbon storage.

1. INTRODUCTION

Listvenite (*sensu stricto*) is a fuchsite-quartz-carbonate assemblage produced by alteration of ultramafic rocks (Halls and Zhao, 1995), but the term has been broadly applied to include many other carbonate-rich alteration products of ultramafic rocks. In this paper, we use the term to refer to rocks composed almost entirely of quartz + magnesite and/or dolomite, formed by CO₂-metasomatism of peridotite. Listvenite deposits initially attracted attention for their association with gold mineralization and other economically-valuable hydrothermal deposits (Rose, 1837), but more recently have been highlighted as a natural analog to mineral carbon storage (Hansen et al., 2005; Kelemen et al., 2011; Beinlich et al., 2012).

Other carbonated peridotite lithologies can be found throughout the Samail

ophiolite. Previous studies have highlighted the geologically rapid ongoing formation of carbonate veins and travertine deposits in association with low-temperature alteration of peridotite as a promising example of the potential for enhanced *in situ* mineral carbonation of peridotite to provide an effective method of permanent carbon storage (e.g., Kelemen and Matter, 2008). While ongoing low-temperature carbonation processes provide useful information about carbonation rates and the propagation of carbonate veins, listvenites provide an opportunity to understand the conditions under which complete carbonation of peridotite can be achieved. Other highly carbonated products of peridotite alteration, such as magnesite-talc “soapstone” are also exist in Oman, and some comparisons between partially carbonated peridotite lithologies and listvenite in Oman can be found in the Electronic Supplement, section S.1.

The presence of listvenite near the base of the Samail ophiolite has been noted by several researchers (Glennie et al., 1974; Stanger, 1985; Villey et al., 1986; Wilde et al., 2002; Nasir et al., 2007; Kelemen et al., 2011), but there has been no consensus on a model for the formation of listvenite in Oman. Referred to as alternatively as “Amqat,” birbirit, silicified serpentinite, listwaenite, or listwanite, these rocks have been proposed to have formed by leaching of magnesium under tropical weathering conditions in the late Tertiary (Glennie et al., 1974), reaction with warm groundwater during Paleogene faulting (Stanger, 1985; Wilde et al., 2002), and reaction with sediment-derived fluids during emplacement of the ophiolite (Kelemen et al., 2011). We present geochemical data from Oman listvenites to provide constraints on the timing, temperature, fluid composition, and fluid sources for listvenite formation.

We collected listvenite and nearby metasediment and serpentinitized peridotite from

75 a large antiform comprising a ridge crest just north of Wadi Mansah, 12 km southeast of
76 Fanjah. A list of sample locations and descriptions can be found in Supplementary Table
77 S1. The location of our field area within the Samail ophiolite is shown in Figure 1, and a
78 geologic map of this locality is presented in Figure 2. In Wadi Mansah, listvenite forms
79 10 to ~ 200 meter thick bands roughly parallel to banding in the host peridotite (pictured
80 in Figure 3). Beneath the listvenites and their host peridotite are minor amphibolites,
81 greenschist facies metabasalts and chert, plus more extensive sections of
82 metasedimentary phyllites containing quartz, calcite, clinochlore, illite and muscovite.
83 These lithologies are part of the metamorphic sole of the ophiolite (Villey et al., 1986). In
84 turn, beneath the metamorphic sole are diagenetically modified sediments of the
85 Hawasina group (Villey et al., 1986).

86 Our field area falls within the region of detailed mapping of the “Amqat”
87 occurrence described by Stanger (1985) and is located within a few kilometers of the
88 listvenite outcrops described by Wilde et al. (2002). However, many of the listvenite
89 samples we collected at these localities are not consistent with previous descriptions of
90 listvenite from this region. Lithologies interpreted as listvenites in previous studies from
91 this area include highly silicified serpentinite containing only minor dolomite and/or
92 calcite (Glennie et al., 1974; Stanger, 1985; Wilde et al., 2002; Nasir et al., 2007), and
93 carbonate-dominated listvenite composed of dolomite and/or calcite with accessory
94 fuchsite, chlorite, quartz, barite and oxides (Nasir et al., 2007). The listvenite in Wadi
95 Mansah differs from samples described in these previous studies in the predominance of
96 magnesite. The magnesite + quartz assemblage that typifies listvenite at the Wadi
97 Mansah locality reflects carbonation of peridotite with relatively little change to the bulk

composition beyond the addition of CO₂, whereas other listvenite bodies in Oman are dominated by dolomite and calcite (e.g., Stanger, 1985; Wilde et al., 2002; Nasir et al., 2007).

2. METHODS

2.1 Compositional analyses

The mineralogical and elemental compositions of samples were studied by petrographic microscope, powder X-ray diffraction (XRD), X-ray fluorescence (XRF), and electron microprobe. Powdered samples were analyzed by XRD using a Panalytical X'Pert powder X-ray diffractometer at Lamont-Doherty Earth Observatory and peaks for constituent minerals were identified using MacDiff (Petschick, 2001) and Match! software (Brandenburg and Putz, 2009). Whole rock major and trace element composition were determined by XRF at the Washington State University GeoAnalytical Lab, where loss on ignition (LOI), primarily due to volatilization of H₂O + CO₂, was also measured (<http://environment.wsu.edu/facilities/geolab/>). Back-scattered electron images and major element composition of phases in polished thin sections were obtained using a 5-spectrometer Cameca SX-100 electron microprobe located at the American Museum of Natural History in New York. Carbonate and silicate mineralogy of listvenite samples, identified by optical petrography, XRD and EMPA, are included in Table 1. Bulk rock compositions by XRF are shown in Supplementary Table S4. Summary electron microprobe data are presented in Supplementary Tables S7-S12.

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122 **2.2 Sr isotopes and isotopic dating**

123 Sr isotopic analyses were completed at Lamont-Doherty Earth Observatory, using a
124 VG Sector 54 multi-collector thermal ionization mass spectrometer (TIMS). Bulk Sr
125 isotope ratios were measured in listvenites and underlying allochthonous
126 metasedimentary and metavolcanic rocks from Wadi Mansah. Mineral separation for
127 determination of an internal Rb-Sr mineral isochron in sample OM10-26 was partially
128 achieved by magnetic separation of sieved grains liberated by self-fragmentation under
129 high voltage (Selfrag). Although the fine-grained nature of these rocks and variable
130 mineral compositions prevented complete separation of minerals, eight fractions with
131 variable proportions of quartz, magnesite, and fuchsite were obtained and analyzed for Sr
132 isotopic ratios. Rb:Sr ratios for Rb-Sr dating were analyzed by inductively coupled
133 plasma mass spectrometry (ICP-MS) measured on a VG PlasmaQuad Excell ICPMS.
134 Summary Sr isotopic data are presented in Supplementary Tables S13 and S14.

135

136 **2.3 Carbonate clumped isotopes**

137 The carbonate clumped isotope paleothermometer is based on the temperature-
138 dependent abundance of ^{13}C - ^{18}O bonds in carbonate minerals relative to a stochastic
139 distribution. The extent of “clumping” of ^{13}C and ^{18}O is quantified using the variable
140 $\Delta 47$, which measures the excess of mass-47 CO_2 (primarily $^{13}\text{C}^{18}\text{O}^{16}\text{O}$) relative to the
141 abundance expected for stochastic distribution of the same bulk isotopic composition
142 (Wang et al., 2004). $\Delta 47$ values are positively correlated with $1/T^2$, where T is the
143 temperature of carbonate formation in Kelvin (Ghosh et al., 2006). Unlike conventional

stable isotope thermometers, clumped isotope thermometry does not depend on the isotopic composition of the fluid from which the carbonate was precipitated, making it useful in ancient terrestrial and low-temperature hydrothermal environments (Eiler, 2011).

Clumped isotopic data were obtained on magnesite, dolomite, and calcite from listvenite and underlying allochthonous metasediments from Wadi Mansah. All samples were analyzed at the California Institute of Technology (Caltech), over two sessions in 2011 and 2012. To validate the application of clumped isotope thermometry to magnesite, magnesite samples formed at known temperatures were also analyzed. These included synthetic magnesite samples grown at temperatures of 40-250°C (Deelman, 1999; Hänchen et al., 2008; Saldi et al., 2010; Saldi et al., 2012); natural playa magnesite from Atlin, British Columbia formed at ~3-10°C (Power et al., 2014); magnesite + quartz listvenite from Atlin, British Columbia, with fluid inclusion temperatures of 210-180°C (Andrew, 1985; Hansen et al., 2005); and a magnesite-bearing metaperidotite from Val d'Efra, Switzerland, formed during Barrovian regional metamorphism at temperatures of $645 \pm 10^\circ\text{C}$ (Ferry et al., 2005). Results of this magnesite calibration are presented in the Electronic Supplement (Supplementary Table S2, Supplementary Figure S4).

Crushed and sieved (150-250 μm) dolomite and calcite samples were reacted using the automated online extraction system described in Passey et al. (2010), wherein samples are reacted for 20 minutes in a common phosphoric acid bath maintained at 90°C with continuous cryogenic trapping of evolved CO_2 followed by further automated cryogenic and GC purification. Crushed and sieved (150-250 μm) magnesite samples digested offline in phosphoric acid at 90°C in sealed reaction vessels for 17 hours. To

avoid contamination from coexisting dolomite, CO₂ evolved from magnesite in the first 20 minutes of phosphoric acid digestion was discarded.

Carbon, oxygen, and clumped isotope ratios were measured on a Thermo Finnigan MAT 253 gas source mass spectrometer at Caltech, employing standard configurations and methods (Huntington et al., 2009; Passey et al., 2010). Heated gas samples were analyzed daily to correct for instrument nonlinearity and scale compression, allowing data to be normalized to the stochastic reference frame used for the original calibration of the clumped isotope thermometer reported in Ghosh et al. (2006). Following heated gas normalization, the empirically derived acid fractionation correction of +0.081‰ was added to $\Delta 47$ data to account for the difference between the phosphoric acid temperature of 90°C used in this study and the phosphoric acid temperature of 25°C used by Ghosh et al. (2006) in the original calibration (Passey et al., 2010). Clumped isotope data were converted from the Caltech reference frame to the absolute reference frame of Dennis et al. (2011) using a transfer function derived from heated gases and calcite standards analyzed over these two sessions (see Supplementary Table S3). Average clumped isotope data are presented in Table 2, and all clumped isotope data are presented in Supplementary Table S2.

2.4 Oxygen isotopes in quartz

$\delta^{18}\text{O}$ was measured in quartz separates from nine listvenite samples in which clumped isotope compositions were also analyzed. Crushed and sieved samples were magnetically separated, treated with HCl and oxalic acid to remove carbonate and iron oxides, and picked under a microscope. Quartz $\delta^{18}\text{O}$ measurements were performed on a

Thermo MAT 253 mass spectrometer at the Earth Systems Center for Stable Isotopic Studies (ESCSIS) at Yale University, using CO₂ laser fluorination techniques. Measured sample $\delta^{18}\text{O}$ values were standardized to Gore Mountain Garnet ($\delta^{18}\text{O} = 5.8\text{‰}$ SMOW) and NBS28 quartz standards ($\delta^{18}\text{O} = 9.6\text{‰}$ SMOW). Results of quartz $\delta^{18}\text{O}$ analyses are shown in Supplementary Table S5.

3. RESULTS

3.1 Mineralogy and Petrology

Optical microscopy, XRD, and electron microprobe analyses reveal that our listvenite samples are predominantly composed of magnesite and/or dolomite + quartz, with minor Fe-oxides, relict chromian spinels and local fuchsite. In ~10m thick listvenite bands occurring within partially serpentinized peridotite, the carbonate is almost exclusively magnesite (“magnesite-quartz listvenite”), while in an overlying ~100m thick body of listvenite that makes up the crest of the antiform along Wadi Mansah, the carbonate is frequently dolomite (“dolomite-quartz listvenite”), though magnesite is also found in this section of the outcrop. In samples collected from “listvenite-serpentinite transition zones”, antigorite ± talc ± chlorite are the dominant silicate phases rather than quartz. Table 1 lists mineral parageneses observed in listvenites and associated rocks. Average mineral compositions from electron microprobe analyses are provided in Supplementary Tables S7-S12.

In listvenites from Wadi Mansah, cross-cutting relationships suggest quartz and carbonate are coeval. Carbonate (either dolomite or magnesite) and quartz are finely

213 intergrown, frequently down to micron scale. In addition to fine-grained matrix material,
214 carbonate and quartz form hierarchical vein networks, in which quartz veins cut and are
215 also cut by carbonate veins at micrometer to centimeter scales (Figures 4 and 5). Minor
216 dolomite and calcite occur in some magnesite-quartz listvenite as cross-cutting veins and
217 vugs (e.g., Figure 4). While carbonates from the active, low-temperature alteration
218 system in Oman have <0.5 wt% FeO (Streit et al., 2012), magnesite and dolomite from
219 Oman listvenites have a molar Mg# ($\text{Mg}/(\text{Mg}+\text{Fe})$) of ~ 0.95 on average (~ 5 wt% FeO in
220 magnesite, ~ 2 wt% in dolomite; see Supplementary Table S7). A more detailed
221 discussion of iron partitioning between carbonate and magnesium silicate phases in
222 listvenites and other carbonated peridotite lithologies in Oman can be found in the
223 Electronic Supplement (Supplementary Figure S2 and related text in Section S.1).

224 Unlike serpentinitized peridotite in Oman far from listvenites (e.g., Boudier et al.,
225 2010; Streit et al., 2012), serpentine in the listvenite-serpentinite transition zones at the
226 margins of listvenite bodies is primarily antigorite rather than lizardite or chrysotile,
227 though XRD suggests all three polytypes may be present in these samples. In these
228 samples from the listvenite margin, antigorite coexists with chlorite, talc, and/or quartz
229 (Figure 5c-e). In contrast, serpentinites 1-3 m away from the listvenite margin are ~ 30 -
230 100% serpentinitized, with mesh-texture lizardite and chrysotile surrounding relict olivine
231 (“partially serpentinitized peridotite”). In the listvenite-serpentinite transition zones from
232 the listvenite margin and in partially serpentinitized peridotite occurring 1-3 m away from
233 the listvenite, serpentine has an average Mg# of ~ 95 (Supplementary Table S8), which is
234 the value expected for antigorite in Fe/Mg exchange equilibrium (Trommsdorff and
235 Evans, 1972) with local relict olivine (Supplementary Table S9), similar to typical mantle

olivine from the Samail ophiolite with an Mg# of 91 (Hanghøj et al., 2010). In some of the partially serpentinized samples near the listvenite, the mesh is defined by this Mg# ~95 serpentine, but more Fe-rich serpentine (e.g., Mg# ~85) rims or completely replaces relict olivine in the mesh cores (Supplementary Figure S3).

Iron oxides are abundant in listvenite, samples from the listvenite-serpentinite transition zones, and partially serpentinized peridotite. In the listvenite-serpentinite transition zones and in partially serpentinized peridotite, fine-grained magnetite is present in disseminated patches, irregular veins, and larger aggregates (up to 30 μm) rimming Cr-spinels. In fully carbonated listvenites, iron-rich phases include fine-grained hematite and extremely fine-grained, unidentified iron oxides/hydroxides. Fine-grained hematite (<10-20 μm) occurs as isolated needles, veinlets, rims on Cr-spinels, and subhedral-to-euhedral grains in listvenite. Electron microprobe analyses of the unidentified iron-rich phase yield average totals of ~78-88 wt% and indicate ~5 wt% SiO_2 even when the iron phase occurs within pure carbonate veins and is analyzed with a 1 μm beam diameter (Supplementary Table S10). Fe K-edge X-ray absorption edge spectra (XANES) on one listvenite containing this fine-grained iron phase collected by collaborators A. Templeton and L. Mayhew at University of Colorado Boulder are unique among their large library of model compounds, but are most similar to amorphous Fe(III)-oxide microbial mat spectra from low-temperature submarine hydrothermal vents (Templeton et al., 2009; Toner et al., 2012). Thus the identity of host phase for much of the iron in listvenite remains unclear.

Relict chromian spinels are common in listvenites from Wadi Mansah, and in many cases serve as the clearest indication of a peridotite protolith in these otherwise dramatically transformed rocks. Although Cr-spinel is typically the only relict phase

remaining from the protolith, even these spinels have experienced significant alteration, with relatively MgAl_2O_4 -rich end-members typical of Oman harzburgite present only in partially serpentinized peridotites and the least-altered cores of spinels in some listvenite samples (Supplementary Table S11). Most spinel analyses from listvenite samples have much lower Mg# (average ~30) and higher Cr# (molar $\text{Cr}/(\text{Cr}+\text{Al})$, average ~80) than spinel from fresh Oman peridotite (average Mg# ~60 in harzburgite, ~50 in dunite; average Cr# ~50 in harzburgite, ~60 in dunite) (Hanghøj et al., 2010), as is typical for spinels affected by hydrothermal alteration (e.g., Evans and Frost, 1975; Kimball, 1990; Mellini, 2005).

Fuchsite (Cr-rich muscovite) occurs in trace quantities in a few samples, and in minor quantities (roughly 5%) in only one sample, OM10-26 (Table 1). Fuchsite occurs in mm-scale bright bluish-green spots composed primarily of quartz intergrown with minor amounts of very fine-grained fuchsite. Larger fuchsite grains in OM10-26 pseudomorphically replace Cr-spinel (Supplementary Figure S6), which is not present as relicts in this sample, unlike most other samples. Fuchsite compositions in this sample trend toward the Mg# and Cr# of Cr-rich spinels in listvenites (Supplementary Figure S7).

3. 2 Bulk compositions

Listvenite bulk compositions, at the cubic meter scale, generally approximate the compositions of average Oman harzburgite (Godard et al., 2000; Hanghøj et al., 2010) with addition of CO_2 and in many cases Ca. A full table of bulk rock compositions by XRF can be found in Supplementary Table S4. While other studies have noted a high

degree of silicification in some Oman listvenites (e.g., Stanger, 1985; Wilde et al., 2002), we find similar numbers of samples showing silica gains and losses, with silica content least variable and most similar to Oman harzburgite in the listvenite-serpentinite transition zones and in the magnesite-quartz listvenites (Figure 4). Mg contents and Mg# in these two types of rocks (Figure 6a,c) are also in the range of those of Oman harzburgite. The abundance of quartz veins makes it clear that silica was mobilized in the system. The relatively high Mg-numbers of quartz-rich samples (Figure 6c) suggest that the high proportion of silica in those samples is primarily due to addition of Si (at the hand sample scale) rather than loss of Mg. Dolomite-quartz listvenites exhibit greater compositional variability than their magnesite counterparts, and appear to have lost Mg (Figure 6a) and gained Ca (Figure 6b).

Volatile-free concentrations of minor and trace elements in listvenites are also broadly similar to average partially serpentinized peridotite from our mapping area and from other areas of the Samail ophiolite (Figure 7, Supplementary Table S4), with the most notable exceptions being minor addition of potassium in most listvenites, and addition of manganese in most dolomite-bearing listvenites. Figure 7 further illustrates the calcium gain and magnesium loss experienced by dolomite-listvenites, and also shows that volatile-free major and trace element bulk compositions of magnesite-quartz listvenites are frequently the same, within error, as average Oman harzburgite for all elements for which our XRF data can be compared with the data from Hanghoj et al. (2010). The isochemical nature of magnesite-listvenite formation during peridotite carbonation is also illustrated in selected “isocon” plots in Supplementary Figure S5.

3.3 Sr isotopic compositions

Bulk strontium isotopic ratios for listvenites and underlying allochthonous metasediments and metavolcanics are presented Figure 8 and Supplementary Table S13. Measured $^{87}\text{Sr}/^{86}\text{Sr}$ values in the listvenite range from 0.7095 to 0.7135. Sr isotopic ratios probably remained largely unchanged over time due to low Rb content. Most of these Sr isotopic ratios are significantly higher than in Cretaceous to modern seawater (Veizer et al., 1999), and are consistent with our new values within the underlying allochthonous metasediments, which range from 0.7061 to 0.7189 (corresponding to values of 0.7061-0.7122 at 96 Ma during emplacement of the ophiolite, (Hacker et al., 1996)). Even more radiogenic strontium isotope ratios have been reported in autochthonous clastic sediments, with $^{87}\text{Sr}/^{86}\text{Sr}$ values up to 0.772 (Weyhenmeyer, 2000).

The presence of K-bearing fuchsite in magnesite-quartz listvenite sample OM10-26 provides a host for Rb, allowing for differential in-growth of ^{87}Sr and construction of an internal isochron (Figure 9, Supplementary Table S14). The data for this sample yield an isochron age of 97 ± 29 Ma, calculated using ISOPLOT, model 3 (Ludwig, 2003). The scatter in these data exceed the expected scatter due to analytical errors, suggesting “geologic” scatter may result from non-uniform initial strontium isotope ratios or later alteration resulting in addition or loss of Rb and/or Sr from some phases¹.

3.4 Stable isotopes

¹ The nominal analytical errors may underestimate the uncertainty of the entire procedure, given that two separate dissolutions of bulk powder of OM10-26 differ in $^{87}\text{Sr}/^{86}\text{Sr}$ by ~ 0.003 , more than two orders of magnitude higher than the standard deviation of filament duplicates prepared from the same dissolution/purification.

$\Delta 47$, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and clumped isotope temperatures in carbonate from listvenite and underlying metasediments are reported in Table 2, and illustrated in Figure 10. A table of all clumped isotope measurements, including known-temperature magnesite samples, standards, and heated gases, is presented in Supplementary Table S2. Clumped isotope temperatures derived from the quadratic fit to all Caltech-derived dolomite and synthetic calcite calibration data employed by Bristow et al. (2011) agreed better with the known temperatures of synthetic magnesite and low temperature playa magnesite than other empirical and theoretical calibrations (Ghosh et al., 2006; Guo et al., 2009; Dennis and Schrag 2010; Dennis et al., 2011; Bristow et al., 2011), as presented in Supplementary Figure S4. The clumped isotope temperatures discussed here are derived using the calibration of Bristow et al. (2011), but results using other calibrations are presented in Supplementary Table S2 for comparison. Measured $\Delta 47$ values correspond to temperatures of 61-114°C for listvenite, 37-71°C for samples from the listvenite-serpentinite transition zones, and 64-171°C for underlying metasediment.

$\delta^{13}\text{C}$ values in listvenite range from -2.5 to +1.0‰ PDB and overlap metasediment values (Fig. 10a,c). Carbonate $\delta^{18}\text{O}$ values range from -9.3 to -6.5‰ PDB in magnesite-quartz listvenite and -11.3 to -4.9‰ PDB in dolomite-quartz listvenite. In the allochthonous metasediments directly underlying the listvenite in Wadi Mansah, $\delta^{18}\text{O}$ values range from -10.0 to -8.9‰ PDB in calcite and are -9.4‰ PDB in dolomite. $\delta^{18}\text{O}$ values in quartz (Supplementary Table S5) range from 21.5 to 23.8‰ SMOW in magnesite-quartz listvenite and from 16.5 to 25.7‰ SMOW in dolomite-quartz listvenite and are correlated with $\delta^{18}\text{O}$ in carbonate (Figure 11).

4. DISCUSSION

4.1 Timing of listvenite formation

The 97 ± 29 Ma Rb-Sr age derived from magnesite-quartz listvenite sample OM10-26 suggests that listvenite formation occurred during emplacement of the ophiolite, which was initiated ~ 96 Ma and continued until ~ 78 Ma (e.g., Hacker et al., 1996; Rioux et al., 2013), rather than during a period of increased heat flow in the early Tertiary (~ 36 -40 Ma) as proposed by Wilde et al. (2002). This age is also consistent with mapping of late Paleocene to Eocene conglomerates unconformably overlying the listvenite (Villey et al., 1986). Although previous workers have hypothesized that listvenite formation in Oman occurred subsequent to obduction, syn-obduction metasomatism has been proposed to explain other listvenite occurrences in ophiolites worldwide (e.g., Buisson and Leblanc, 1987; Plissart et al., 2009).

4.2 Protolith

Listvenite formed from partially serpentinized harzburgites and dunites at and near the base of the mantle section of the Samail Ophiolite. Many samples of magnesite-quartz listvenite overlap entirely the bulk compositions of adjacent partially serpentinized peridotite and of peridotite elsewhere in the ophiolite (Godard et al. 2000; Hanghøj et al., 2010), as shown in Figures 6 and 7. In partially serpentinized peridotite enclosing the listvenite at Wadi Mansah, the degree of serpentinization varies from 30-100%, with relict olivine becoming more abundant with increasing distance from contacts the listvenite. Approximately 30-60% serpentinization likely occurred during initial suboceanic alteration (Boudier et al., 2010) prior to listvenite formation. Whereas early

serpentinization formed mesh-texture lizardite and chrysotile, during subsequent carbonation, antigorite formed in the listvenite-serpentine transition zones, perhaps stabilized by elevated silica activity in the fluid associated with listvenite formation. In serpentinitized peridotite just beyond these transition zones, the high degree of serpentinization suggests that the fluid pathways that allowed for listvenite formation have also facilitated additional hydration of peridotite. In some of our partially-serpentinized peridotite samples, more Fe-rich lizardite (e.g., Mg# ~85) rims or replaces relict olivine in the mesh cores, accounting for ~10% of the serpentine present (Supplementary Figure S3 and related text in Supplementary Section S.1). These limited amounts of low-Mg# serpentine likely represent later, lower-temperature alteration (Streit et al., 2012), superimposed on pre- and syn-obduction serpentinization.

This suggests that 20 to 90% relict olivine may have been available in the protolith prior to listvenite formation. Combined with the observation that many magnesite listvenites have compositions equivalent to mantle harzburgites from the Samail ophiolite + CO₂, with little or no dissolution and removal of other chemical components (Section 3.2), these data imply very large volume changes during listvenite formation. For example, the volume increase for the reaction forsterite + 2 CO₂ = 2 magnesite + quartz, computed as the difference between product volume – reactant volume divided by the reactant volume, is approximately 80%.

4.3 Temperature constraints

We derive temperature constraints for the formation of listvenite from mineral parageneses (80-130°C) and clumped isotopes (average = 90°C), consistent with oxygen

isotopes in carbonate and quartz for fluid $\delta^{18}\text{O}$ values near 0‰ SMOW. Most of the temperatures recorded by our listvenite samples are warmer than the inferred maximum temperatures of ~65°C for listvenite formation proposed by Wilde et al. (2002), and significantly cooler than temperature estimates for other listvenite bodies worldwide: about 210-280°C in Canada (Madu et al., 1990; Schandl and Wicks, 1993; Schandl and Gorton 2012; Andrew, 1985), 280-340°C in Armenia (Spiridonov, 1991), 200-300°C in eastern Australia (Oskierski et al., 2013), 250-350°C in California (Weir and Kerrick, 1987), and 150-250°C in Morocco (Buisson and Leblanc, 1987).

4.3.1 Temperatures from mineral parageneses

The similarity of the volatile-free bulk compositions of magnesite-quartz listvenites to those of relatively unaltered Oman harzburgites suggests a relatively simple alteration history, allowing us to make inferences about the conditions of peridotite carbonation. Temperature- X_{CO_2} phase diagrams (where X_{CO_2} indicates mole fraction $\text{CO}_2/(\text{H}_2\text{O} + \text{CO}_2)$) for the $\text{MgO-SiO}_2\text{-H}_2\text{O-CO}_2$ system (e.g., Figure 12) were calculated at pressures of 1 MPa to 10 GPa using THERMOCALC (Holland and Powell, 1998; Holland and Powell, 2011) to examine the regions of stability for the assemblages observed in listvenite (magnesite + quartz) and in the listvenite-serpentine transition zones (magnesite + talc + antigorite, quartz + talc + antigorite, quartz + antigorite). Using THERMOCALC, the reaction $\text{antigorite} + 30 \text{ quartz} = 16 \text{ talc} + 15 \text{ H}_2\text{O}$ is calculated to occur at temperatures of $\sim 80 \pm 3^\circ\text{C}$ for pressures between 1 MPa and 1 GPa. As for the reaction $\text{chrysotile} + 2 \text{ quartz} = \text{talc} + \text{H}_2\text{O}$ (Streit et al., 2012), the calculated temperature of the reaction $\text{antigorite} + 30 \text{ quartz} = 16 \text{ talc} + 15 \text{ H}_2\text{O}$ reaction is higher ($\sim 130 \pm 15^\circ\text{C}$)

if the thermodynamic database of Gottschalk (1997) is used rather than that of Holland and Powell (2011). The primary effect of increasing pressure is to shift phase boundaries involving magnesite to lower X_{CO_2} (e.g., Figure 13).

The occurrence antigorite + quartz + talc in the listvenite-serpentinite transition zones (e.g., Figure 5d,e) thus provides a temperature estimate of 80-130°C for the margin of the listvenite bands. This also provides constraints for the temperature of listvenite formation, as it is unlikely that a strong thermal gradient was maintained across the <2 m wide transition zone between listvenite and partially serpentinized peridotite. The change in parageneses, from magnesite + quartz to antigorite + quartz ($\pm$ talc, $\pm$ carbonate minerals) can be understood in terms of a decrease in X_{CO_2} in the fluid across the listvenite boundary. Near the temperature of the invariant point, the range of CO_2 concentrations over which talc + magnesite is stable without serpentine is very small, so if temperature and X_{CO_2} were restricted to a relatively small range near the invariant point during alteration, this could explain why talc is not observed without coexisting serpentine in association with the listvenite bodies at Wadi Mansah.

4.3.2 Temperatures from clumped isotope thermometry and oxygen isotopes

Average clumped isotope temperatures in listvenite ($90 \pm 15^\circ\text{C}$) agree well with the petrological temperature estimates of 80-130°C for the antigorite + 30 quartz = 16 talc + 15 H_2O reaction. These temperatures are significantly lower than clumped isotope temperatures recorded by calcite-bearing metasediments within ~100m of the basal thrust beneath the listvenite (~160°C). These metasediments are mapped as part of the metamorphic sole, some of which experienced peak temperatures as high as 800°C in the

early stages of emplacement of the ophiolite (Ghent and Stout 1981). The clumped isotope temperatures in the calcite-bearing metasediments may represent closure temperatures, as clumped isotope closure temperatures range from ~150-250°C in marbles and carbonatites (Dennis and Schrag, 2010).

Although clumped isotope temperatures in listvenite are broadly in agreement with petrological temperature estimates, the broad range of $\Delta 47$ values from listvenite samples, compared with the narrower range of $\delta^{18}\text{O}$ values in both carbonate and quartz, suggests that some $\Delta 47$ values may have been subject to bond re-ordering after the initial precipitation of the carbonate, or that carbonates in our samples are polygenetic, recording several episodes of formation or recrystallization. For example, the relative standard deviation of clumped isotope temperatures in magnesite listvenites is 16%, while the relative standard deviation of temperatures derived from conventional carbonate-water oxygen isotope thermometry in those same samples is only 7% (average temperature $110 \pm 7^\circ\text{C}$) calculated using magnesite-water oxygen isotope fractionation factors from Chacko and Deines (2008) and an assumed fluid $\delta^{18}\text{O}$ of 0‰ SMOW (Supplementary Table S6).

The clumped isotope signal could have been modified by multiple episodes of formation and/or recrystallization of carbonates in our samples, over a range of temperatures. For example, minor late precipitation of carbonates and/or recrystallization could have occurred during low temperature, post-emplacement interaction with groundwater. Mixing of CO_2 derived from this younger, low temperature component with CO_2 derived from carbonate precipitated during listvenite formation could lead to anomalous $\Delta 47$ values. Mixing of CO_2 from carbonates with different $\delta^{13}\text{C}$ and/or $\delta^{18}\text{O}$

may result in a $\Delta 47$ value of the mixture that is not only non-linear with respect to the weighted proportions of the endmembers, but that is outside the range of $\Delta 47$ values of the two endmembers (Eiler and Schauble 2004). The highest $\Delta 47$ values we observe in listvenite correspond to the lowest $\delta^{13}\text{C}$ values, so it is possible that these high $\Delta 47$ values are artificially high as the result of non-linear mixing with a carbonate precipitated from a source with low $\delta^{13}\text{C}$, such as meteoric water for example.

Regardless of mechanisms that may have generated higher $\Delta 47$ values in some samples, all but two of the clumped isotope temperatures in listvenite and the listvenite-serpentine transition zones fall between 70 and 115°C, similar to temperatures estimated from mineral parageneses in the transition zones.

Carbonate-quartz oxygen isotope fractionations cannot provide reliable temperature estimates in our listvenite samples, due in part to a lack of temperature sensitivity and uncertainty in the fractionation factors for magnesite and dolomite. However, carbonate and quartz appear to be isotopic equilibrium in most samples (at least for some choices of fractionation factors), and temperatures derived from oxygen isotope fractionation between water with assumed $\delta^{18}\text{O}$ values near 0‰ SMOW and magnesite, dolomite, or quartz from listvenite generally overlap with those derived from mineral parageneses and clumped isotope thermometry (see Supplementary Table S6). Additional discussion of carbonate and quartz $\delta^{18}\text{O}$ and related tables and figures can be found in the Electronic Supplement (Supplementary Tables S5 and S6, Supplementary Figure S8, and related text in Supplementary Section S.4).

4.4 Fluid sources for listvenite formation

Sr isotope values can be viewed as a tracer for Sr from the source of the CO₂-bearing fluids that formed listvenites, and by association, for Ca and other elements that were also enriched during formation of listvenites. In Quaternary low-temperature carbonate veins in serpentinite and travertine from the Samail ophiolite, ⁸⁷Sr/⁸⁶Sr is higher than mantle values but less than or equal to modern seawater values, suggesting that Sr in those rocks was derived from a combination of (a) seawater, meteoric water, or ground water in Oman with ⁸⁷Sr/⁸⁶Sr ≤ 0.709 (Weyhenmeyer, 2000) and (b) mantle Sr with ⁸⁷Sr/⁸⁶Sr extending down to 0.703 (Gerbert-Gaillard, 2002; see data compilation in Kelemen et al., 2011, Supplementary Figure 3 and associated text). By contrast, the age corrected Sr isotopic ratios of listvenites (0.7092-0.7135 ⁸⁷Sr/⁸⁶Sr at 96 Ma) must include substantial Sr from sources that had ⁸⁷Sr/⁸⁶Sr higher than seawater. Our samples of allochthonous metasediments directly underlying the listvenite at the Wadi Mansah locality include several suitably radiogenic sources (⁸⁷Sr/⁸⁶Sr up to 0.7122 at 96 Ma). Sr may also have been derived from underlying autochthonous sediments, which include even more radiogenic clastic sediments with ⁸⁷Sr/⁸⁶Sr ~0.72-0.77 at 96 Ma (Weyhenmeyer et al., 2000). (See Figure 8.) Carbonate δ¹³C from listvenites and metasediments from Wadi Mansah also overlap, with most values between 2.5 and +1‰ PBD, supporting a sediment-derived source of carbon in the listvenite (Figure 10a,c).

The fluid mediating Sr, CO₂, Ca, and K transfer could have been derived from sediment-equilibrated seawater released upon compaction of pore space, or from devolatilization of hydrous minerals in sediments. This would also be consistent with stable isotope data. Assuming the temperatures indicated by mineral paragenesis and the highest recorded clumped isotope temperatures are most representative of the temperature

of listvenite formation, $\delta^{18}\text{O}$ compositions of carbonate and quartz in listvenite would be in equilibrium with average fluid $\delta^{18}\text{O}$ values ranging from about $-1 \pm 3\text{‰}$ at 80°C to $5 \pm 3\text{‰}$ at 130°C . The variability in these fluid $\delta^{18}\text{O}$ values averaged over all samples and choices of fractionation factors is due to both variability between samples and variability between available fractionation factors. (See Supplementary Figure S8 and related text in Supplementary Section S.4 for additional details on $\delta^{18}\text{O}$ in listvenites.) The $\delta^{18}\text{O}$ of Cretaceous seawater in sedimentary pore space would evolve to about 5 to 8‰ if it were fully equilibrated with authigenic calcite and to about -8 to -5‰ if it were fully equilibrated with clastic quartz². Thus, the listvenite $\delta^{18}\text{O}$ values are within the range expected for fluid derived from subducting sediments.

The formation of listvenite during the emplacement of the Samail ophiolite provides a window into CO_2 metasomatism in the shallow hanging wall of subduction zones. Along typical subduction zone geotherms, slab-top temperatures around $80\text{--}130^\circ\text{C}$ are reached at depths of $\sim 10\text{--}50$ km (e.g., Rüpke et al., 2004; Syracuse et al., 2010). Listvenite a few hundred meters above the basal thrust would experience higher temperatures, making these maximum depth estimates for the formation of the listvenite. Thus, it is likely that listvenite formation occurred at pressures of roughly 0.2-1.5 GPa. Geological data also provide constraints on pressure. The crustal section of the Samail ophiolite, overlying mantle peridotites, is 5-7km thick (Nicolas et al., 2000). The mantle section of the ophiolite, overlying the basal thrust, had a variable thickness and is up to 15 km thick in present day sections (e.g., Boudier and Coleman, 1981). This yields a

² assuming an initial temperature of 10°C ; initial $\delta^{18}\text{O}$ of -1‰ for seawater, 31‰ for calcite, 6‰ for quartz; initial porosity of 0.70; final temperature of $80\text{--}130^\circ\text{C}$; final porosity of 0.5; and mineral-water fractionation factors from Friedman and O'Neil (1977)

combined thickness of 5 to 22 km (0.1-0.7 GPa) for the section overlying the Wadi Mansah listvenites at the time of their formation.

At pressures between 0.2 and 1.5 GPa, high concentrations of CO₂ in the fluid are not required to stabilize magnesite-quartz listvenites (Figure 13). The minimum mole fraction of CO₂ necessary to stabilize magnesite + quartz at temperatures of 80-130°C varies from X_{CO2} ~10⁻⁸-10⁻⁷ at 1.5 GPa to X_{CO2} ~10⁻⁵-10⁻⁴ at 0.2 GPa. If listvenite formation occurred during emplacement of the ophiolite and the antigorite-quartz-talc assemblage observed at the margins of the listvenite body is indicative of peak temperatures, then Cretaceous seawater CO₂ concentrations, equivalent to X_{CO2} ~10⁻⁴ (Wallman, 2001), would be sufficient to stabilize magnesite + quartz. In contrast, formation of listvenite via low pressure alteration involving shallow groundwater, as suggested by Stanger (1985) and Wilde et al. (2002), would require a more CO₂-rich fluid (e.g., X_{CO2} ~10⁻² at 1 MPa) at similar temperatures. It should be noted that the approach to thermodynamic modeling and choice of thermodynamic databases can have a significant effect on the calculated CO₂ concentrations required to stabilize the magnesite + quartz assemblage. For example, Klein and Garrido (2011) investigated phase equilibria in the MgO–SiO₂–H₂O–CO₂ system through reaction path models of reaction between serpentinite or dunite and CO₂-enriched seawater at 50 MPa, using the software packages SUPCRT92 (Johnson et al., 1992) and EQ3/6 (Wolery, 1992). In their models, the boundary between magnesite + quartz and talc + quartz at 100°C occurred at a CO₂ activity of 10^{-2.5}, whereas our THERMOCALC calculations (Figure 13) place this boundary at X_{CO2} of 10^{-4.3} at 100°C and 50 MPa.

Metamorphic decarbonation of sediments is not expected to occur beneath the forearc in subduction zones (e.g., Kerrick and Connolly, 2001; Gorman et al., 2006). However, carbonate dissolution from metasediments in aqueous fluids has been shown to be a source of CO₂ for metasomatic processes in subduction zones (e.g., Sakai et al., 1990; Haggerty, 1991; Mottl et al., 2004; Konno et al., 2006; Lupton et al., 2006; Frezzotti et al., 2011). Carbonate dissolution and release of CO₂-enriched fluids could occur gradually as pore-water in equilibrium with sediments is released during compaction, or more suddenly as fresh water is released via dehydration of minerals in the sediments and reacts with carbonate-bearing sediments, for example during the smectite to illite transition at ~ 75 to 150°C (Lynch 1997). The resulting fluid, saturated in the minerals in the sedimentary host rock, would rise into the overlying mantle, perhaps migrating first along the top of the subducting plate or along faults subparallel to the top of the plate. Focusing of fluid flow could yield localized, high fluid fluxes. Seafloor fluid expulsion in forearcs demonstrates that water released by dehydration of subducted sediments is transported both vertically and trench-ward by deep-seated thrust faults (Hensen et al., 2004). In Oman, listvenite follows major fault zones, and the antiformal structure of the Wadi Mansah locality, if present during carbonation, could also have localized fluid flow.

Rough mass balance calculations show that the flux of CO₂-bearing fluid from the subducted sediments would be sufficient for the formation of the extensive listvenites observed in Oman. A 100-meter thick column of listvenite containing 30 wt% CO₂ contains $\sim 2.5 \times 10^4$ kg C/m². If we assume the carbon concentration in the pore fluid was ~100 ppm (Cretaceous seawater (Wallman, 2001)), then the mass of sediment-derived

fluid reacted to form this listvenite would be at least $\sim 2.5 \times 10^8 \text{ kg/m}^2$, or $\sim 12 \text{ kg/yr/m}^2$ if averaged over $\sim 20 \text{ Ma}$ of obduction (Hacker et al., 1996).

In the case of pore water release, sediments start with a pore volume fraction of ~ 0.4 - 0.7 , and after rapid compaction to ~ 0.2 porosity in the first few kilometers of burial (or subduction), porosity decreases by $\sim 0.04/\text{km}$, yielding $\sim 1.4 \text{ wt\% water / km}$ (Bond and Kominz, 1984). Thus, for a hypothetical 2-3 km column of sediment (e.g., thickness of the Hawasina sediments underlying the Samail Ophiolite) being subducted at a rate of 6 cm/yr , ~ 3 - $5 \text{ kg of pore water/m}^2/\text{yr}$ would be expelled by compaction beneath the overlying mantle. Thus sufficient fluid for observed listvenite thicknesses could be derived from seawater expelled from compacted sediments, particularly if fluids were channelized from a source area 2-4 times the area of the listvenite or if fluids were further enriched in CO_2 during subduction, as calcite solubility should increase with depth (e.g., Dolejs and Manning, 2010; Coto et al., 2012; Kelemen and Manning, 2015).

Mineral dehydration could also contribute CO_2 -bearing fluid. Average global subducting sediment (GLOSS) (Plank and Langmuir, 1998) contains $\sim 7\%$ mineral-bound water, whereas clay-rich, fine-grained clastic sediments contain even more. Release of this water and dissolution of carbonates in sediment could provide an additional source of carbon-bearing fluid for listvenite formation.

Considerable amounts of water can be released by mineral transformations that involve partial dehydration, such as the transformation of clay minerals to micas and chlorite. For example, between 75 and 150°C , the transition of smectite to illite releases $\sim 30 \text{ wt\% H}_2\text{O}$ in mudstones and shales (Lynch, 1997). For a 2-3 km thick sediment section including 50% clay-rich lithologies, subducting at 6 cm/yr , this would produce ~ 2

kg of water/m²/yr. Transformations of hydrated minerals, including expulsion of interlayer water and conversion of opal-A to opal-CT at 30-80°C and expulsion of interlayer water and conversion of smectite to illite at 50-150°C, have previously been proposed as the source of low-chlorinity waters upwelling at serpentine mud volcanoes in the Mariana forearc (Mottl et al., 2004) and at seafloor sites in accretionary prisms (Bebout, 2013).

Additional mineral dehydration and decarbonation are predicted to occur at greater depths in forearc environments (e.g., Rüpke et al., 2004; Gorman et al., 2006). Modeling by Rüpke et al. (2004) indicates that ~50% of the mineral-bound water in sediments should be released by dehydration in a pulse between 30 and 40 km depth. A 3 km column of sediment being subducted at a rate of 6 cm/yr would be expected to release ~8-13 × 10³ kg H₂O/m/yr in this dehydration front. Gorman et al. (2006) predict a pulse of dehydration and decarbonation at ~70-90 km depth, resulting in a fore arc CO₂ flux of 11-37 kg CO₂/m/yr for a 500 m sediment section. If some of these fluids migrated up the subduction zone and then reacted with peridotite at shallower depth, this could also play a role in the formation of listvenite.

In summary, there are at least three viable fluid sources for listvenite formation during emplacement of the Samail Ophiolite and in the shallow hanging wall of subduction zones worldwide: (1) compaction of pore waters from footwall metasediments, (2) low temperature dehydration of opal and clay minerals in footwall metasediments, and (3) higher temperature metamorphic devolatilization reactions coupled with fluid migration up the subduction zone.

4.5 Implications for carbon capture and storage (CCS)

Carbonation of peridotite has been proposed as a method for permanent CO₂ storage (e.g., Seifritz 1990; Lackner et al., 1995) as well as distributed, geological capture of CO₂ (Kelemen and Matter, 2008; Kelemen et al., 2011). Natural analogs to *in situ* mineral carbon sequestration in ultramafic bodies present potential alternatives to *ex situ* mineral carbonation, avoiding the costs of mining, transporting, and treating ultramafic material (e.g., Cipolli et al., 2004; Hansen et al., 2005; Kelemen and Matter, 2008; Kelemen et al., 2011; Beinlich et al., 2012). However, a major concern regarding *in situ* carbonation is that the solid volume increases expected during peridotite carbonation could result in loss of porosity and permeability and armoring of reactive mineral surfaces, thereby limiting reaction progress (e.g., Xu et al., 2004; Hansen et al., 2005).

The presence of listvenite bodies demonstrates that geological carbonation of peridotite can progress to completion under natural conditions. Hansen et al. (2005) and Beinlich et al. (2012) suggest that the smaller solid volume increases associated with carbonation of serpentine rather than olivine reduce the chance of pore space clogging. In Oman, Stanger (1985) proposes that total serpentinization of the basal peridotite preceded formation of the “Amqat” lithology (listvenite). However, we find tens of percent of relict olivine in partially serpentinized peridotite sampled within meters of magnesite-quartz listvenites, as is common in peridotite throughout the mantle section of the ophiolite. These olivine relicts are frequently surrounded by high-Fe serpentine that likely formed later than listvenites, at lower temperatures (Streit et al., 2012), indicating that relict olivine was even more abundant during listvenite formation. In spite of the larger

643 volume increases associated with carbonation of olivine, complete carbonation was
644 attained within the listvenite zones.

645 This solid volume increase may even contribute to reaction progress by
646 maintaining permeability through reaction-driven cracking (e.g., MacDonald and Fyfe
647 1985; Jamtveit et al., 2008; Jamtveit et al., 2009; Rudge et al., 2010; Kelemen et al.,
648 2011; Kelemen and Hirth, 2012; Plümper et al., 2012). Although listvenite bodies in
649 Oman probably follow pre-existing fault zones, and fluid flow may have been localized
650 along such faults, vein orientations in most of our listvenite samples are random or
651 mutually orthogonal, and thus do not appear to be tectonically controlled. Quartz and
652 carbonate veins occur as hierarchical networks extending down to micron scales, forming
653 perpendicular vein sets suggestive of isotropic stresses (e.g., Figures 3b and 5a).
654 Reaction-driven cracking will be favored when reaction rates are high so that stress
655 increases due to volume changes during reaction outpace viscous relaxation. At the
656 inferred conditions of listvenite formation in Oman, ~80-130°C and P_{CO_2} on the order of
657 ~1 to 5 bars (seawater CO_2 concentrations at 0.2 to 1 GPa pressure), the fit of Kelemen
658 and Matter (2008) to experimental data on olivine carbonation (O'Connor et al., 2005;
659 Chizmeshya et al., 2007) yields rates $\sim 10^4$ to 10^5 higher than the carbonation rate at
660 conditions of surficial weathering. These higher reaction rates may have promoted self-
661 fracturing during peridotite carbonation.

662 663 **5. CONCLUSIONS**

664 Mineralogical and isotopic data support the hypothesis that listvenites in Oman
665 formed during obduction of the Samail ophiolite, as CO_2 -enriched fluids derived from

underlying sediments metasomatized hanging wall peridotite. An internal Rb-Sr isochron from one fuchsite-bearing listvenite sample yields an age of 97 ± 29 Ma, consistent with the timing of emplacement of the ophiolite, and with geologic mapping indicating that Late Cretaceous sediments unconformably overlie listvenite. Unlike carbonates formed via ongoing low-temperature alteration of peridotite, age-corrected listvenite Sr isotopic ratios are more radiogenic than seawater, suggesting input of radiogenic Sr from underlying metasediments. Mineral parageneses and carbonate clumped isotope thermometry suggest that listvenite formed at temperatures of 80-130°C. Along a subduction zone geotherm, these temperatures would be reached at ~10-50 km depth, where fluids could be released from subducted sediments either by compaction or partial dehydration reactions. At these pressures, the CO₂ concentration necessary to stabilize the magnesite + quartz assemblage is only slightly higher than seawater CO₂ concentrations. Equilibration of released water with carbonate in subducted sediments can yield fluids with sufficiently high CO₂ concentrations to form magnesite-quartz listvenite upon reaction with hanging wall peridotite, and the mass of fluid produced by compaction and partial dehydration reactions is sufficient to account for the observed mass of listvenite. These calculations are applicable to subduction zones worldwide. Globally, extensive carbonation of mantle wedge peridotite may be more common above subduction zones at the “leading edge of the mantle wedge” than has been previously recognized.

As a natural analog for carbon capture and storage via *in situ* mineral carbonation, listvenite formed in this kind of environment is promising. For example, schemes that involve enhanced convection of seawater through peridotite, rather than injection of high-

P_{CO2} fluids (Kelemen and Matter, 2008; Kelemen et al., 2011) may be expected to achieve complete carbonation of peridotite over time. Even without extremely high CO₂ concentrations, and at temperatures below those corresponding to peak reaction rates in olivine carbonation experiments, complete carbonation of peridotite is attained in nature.

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FIGURE CAPTIONS

Figure 1. Map of the Samail ophiolite in Oman and the UAE, after Lipard et al. (1986).

Small rectangle indicates approximate location of geologic map of Wadi Mansah in

Figure 2.

Figure 2. Geologic map and representative cross-section of the Wadi Mansah listvenite locality, including individual sample locations (place-markers). Compiled from Villey et al. (1986), Google Earth data, and field observations (including hand-held GPS measurements and attitudes of compositional banding and lithological contacts). Map area is between UTM coordinates 2582600 m to 2587150 m N, and 619900 m to 625400 m E, in zone 40 Q.

Figure 3. Listvenite outcrops at Wadi Mansah. (a) listvenite bands enclosed in serpentinitized peridotite; (b) hierarchical quartz and carbonate veins cutting finely intergrown quartz and carbonate; (c) coarse, fracture-filling dolomite on the ridge crest cutting finely intergrown dolomite and quartz.

Figure 4. Cross-cutting relationships between carbonate minerals. (a) Coarse dolomite and calcite veins cut magnesite + quartz listvenite; (b) Brown dolomite-quartz and gray quartz veins cut red magnesite + quartz and white quartz veins, OM09-19.

Figure 5. Micro-textures in samples from transects across the listvenite-serpentinite transition of the main magnesite-quartz listvenite band at Wadi Mansah, back-scattered electron (BSE) images and elemental maps. (a) A representative BSE image of listvenite sample OM09-15 shows fine, intergrown magnesite (dark gray, “mgs”) and quartz cut by dense networks of quartz veins (medium gray, “qtz”). Fine-grained, Fe-oxides (white) are scattered through the matrix, and larger, relict Cr-spinels (very light gray) attest to the peridotite protolith. (b) BSE image of magnesite (dark gray) and quartz (light gray), lacking sharply defined monomineralic vein networks, and intergrown with abundant fine-grained Fe-oxide (white) in listvenite sample OM10-03. (c) Talc-antigorite vein adjacent to magnesite intergrown with antigorite in sample OM10-02 from the listvenite-serpentinite transition zone. Yellow dotted lines are added to emphasize the boundary between talc and antigorite. Although not pictured here, magnesite is also present within these small, mixed talc-antigorite veins. (d) Mixed veins of quartz, talc, and Fe-oxide and dolomite (“dol”) in antigorite (“atg”) in sample OM09-12 from the listvenite-serpentinite transition zone. (e) Bladed antigorite intergrown with quartz in sample OM09-12, shown in an WDS elemental map of Si content (left) and an EDS elemental map of Mg content (right).

Figure 6. (a) Volatile-free molar MgO versus molar SiO₂. (b) Volatile-free molar MgO + CaO versus molar SiO₂. (c) Molar Mg/(Mg + Fe), or Mg#, versus molar SiO₂. Dashed and dotted gray lines show the expected composition of an average peridotite from the Samail ophiolite perturbed only by removal or addition of Mg or Si, respectively. Quartz + magnesite listvenites compositions (red diamonds) and rocks from the listvenite-

serpentine transition zone (green triangles) mostly fall within the range of typical, partially serpentinized peridotite composing the mantle section in the nearby portions of the ophiolite, as represented by the range of data reported by Godard et al. (2000) and Hanghøj et al. (2010) (yellow oval). Dolomite + quartz listvenite compositions (blue squares) span a broader range of Si concentrations and are deficient in Mg, primarily due to variable Ca addition. Low Mg#’s in the dolomite + quartz listvenites could be explained by Mg removal accompanied by Ca addition, and/or by Fe addition.

Figure 7. XRF data from listvenites and associated rocks compared to the composition of fresh harzburgites and dunites from the Samail ophiolite (Godard et al., 2000; Hanghøj et al., 2010). XRF data are projected from loss-on-ignition (LOI), and the volatile-free composition is ratioed to the average composition of partially serpentinized peridotite from Wadi Mansah. The logarithm of these ratios are plotted here, such that a value of zero is identical in composition to that of average partially serpentinized peridotite, positive values indicate enrichments relative to the protolith, and negative values indicate depletions relative to the protolith. Magnesite + quartz listvenite (red), dolomite + quartz listvenite (blue), and samples listvenite-serpentine transition zone (yellow) are similar in composition to partially serpentinized peridotite (green) and fresher harzburgites and dunites from the Samail ophiolite (gray), aside from variable enrichments in Ca, K, and Mn. Most listvenite samples have some enrichment in K (although K is also variable in the protolith). Dolomite + quartz listvenite samples are highly enriched in Ca and moderately enriched in Mn.

Figure 8. Minimum initial Sr isotope ratios for listvenites (red diamonds), local underlying allochthonous metasediments and metavolcanics (yellow circles), and autochthonous clastic metasediments from Weyhenmeyer (2000) (green squares), compared to Sr isotope ratios in modern and Cretaceous seawater (Veizer et al., 1999). Age-corrected Sr isotope ratios were calculated assuming an age of 96 Ma. For the listvenite and local allochthonous metasediments analyzed for this study, the age corrected ratios were calculated using measured $^{87}\text{Sr}/^{86}\text{Sr}$ and Rb:Sr ratios. Rb concentrations were not reported for the autochthonous clastic metasediments from Weyhenmeyer (2000), so an estimated upper bound Rb concentration of 2000 ppm was used with the measured $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr concentration, to estimate a minimum Sr isotope ratio at 96 Ma for these samples.

Figure 9. An internal Rb-Sr isochron constructed from different fractions of varying magnetic susceptibility from magnesite-quartz listvenite OM10-26 yields an age of 97 ± 29 Ma, consistent with the timing of emplacement of the Samail Ophiolite. Age calculated using ISOPLOT model 3 (Ludwig, 2003).

Figure 10. Cross-plots of $\Delta 47$, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and clumped isotope temperature (calculated using calibration of Bristow et al. (2011)) in listvenite and associated lithologies: magnesite + quartz listvenite (red diamonds), dolomite + quartz listvenite (blue diamonds), calcite-bearing metasediment (yellow circles), dolomite-bearing metasediment (blue circle). In part (d), dashed lines indicate the temperature- $\delta^{18}\text{O}$ relationship for magnesite, as calculated by Schauble et al. (2006) for constant fluid $\delta^{18}\text{O}$

ranging from -10 to +30‰ SMOW, as indicated along curves. The slopes of corresponding curves for calcite and dolomite (not plotted) are similar to those for magnesite (e.g., Vasconcelos et al., 2005; Kim and O'Neil, 1997). $\delta^{13}\text{C}$ values cluster within -3 to +1‰, with overlapping values for listvenites and metasediments. Carbonate $\delta^{18}\text{O}$ values in listvenite mostly fall within a range of -5 to -10‰ PDB. If all listvenite samples formed from fluids of similar isotopic composition, these $\delta^{18}\text{O}$ values imply a much narrower range of temperatures than the 37-114°C recorded by clumped isotopes, e.g., ~90-110°C for $\delta^{18}\text{O}_{\text{fluid}} = 0‰$ SMOW and $\delta^{18}\text{O}_{\text{magnesite}}$ between -6 and -10‰ PDB.

Figure 11. $\delta^{18}\text{O}$ values in quartz are correlated with $\delta^{18}\text{O}$ in carbonate (red diamonds = magnesite + quartz listvenite, blue squares = dolomite + quartz listvenite)

Figure 12. Temperature- X_{CO_2} diagram depicting phase equilibria in the $\text{MgO-SiO}_2\text{-H}_2\text{O-CO}_2$ system from 20°C to 220°C at 0.2 GPa. X_{CO_2} = molar CO_2 / (CO_2 + H_2O). Boundaries represent reactions between magnesite (mgs), antigorite (atg), talc (tlc), and quartz (q), calculated using THERMOCALC (Holland and Powell, 1998; 2011). Reactions: (1) $2\text{atg} + 45\text{CO}_2 = 45\text{mag} + 17\text{tlc} + 45\text{H}_2\text{O}$, (2) $3\text{mag} + 4\text{q} + \text{H}_2\text{O} = \text{tlc} + 3\text{CO}_2$, (3) $48\text{mag} + 34\text{q} + 31\text{H}_2\text{O} = \text{atg} + 48\text{CO}_2$, (4) $\text{atg} + 30\text{q} = 16\text{tlc} + 15\text{H}_2\text{O}$.

Figure 13. T- X_{CO_2} phase boundaries for the reaction 3 magnesite + 4 quartz + $\text{H}_2\text{O} = \text{talc} + 3 \text{CO}_2$, calculated in THERMOCALC (Holland and Powell, 1998; 2011) for pressures from 1 MPa to 1.5 GPa.

Table 1. Mineral parageneses (carbonates and silicates)

Sample	Type ^a	Mgs	Dol	Cc	Qtz	Serp	Ol	Tlc	Chl	Fuchs	En	Di
OM09-11	listv.	M			M					tr		
OM09-15	listv.	m	tr	tr	M							
OM09-16	listv.	M	tr		M			m				
OM09-18	listv.	M	tr		M							
OM09-19	listv.	M	M		M							
OM09-20	listv.		M		M							
OM09-27	listv.		M		M							
OM09-28	listv.	M	m		M							
OM09-29	listv.	M	M		M							
OM09-30	listv.	m	M		m							
OM10-03	listv.	M	tr		M							
OM10-09	listv.		M									
OM10-10	listv.		M	m	M							
OM10-11	listv.		M		m							
OM10-12	listv.		M	tr	M							
OM10-14	listv.		M	m	m							
OM10-15	listv.		M	m	m							
OM10-19	listv.		M	m	M							
OM10-20	listv.		M	m	M							
OM10-24	listv.		M	M	m							
OM10-25	listv.	M	m	tr	M							
OM10-26	listv.	M		tr	M				tr	m		
OM09-12	trans.	m	m		m	M		tr	m			
OM10-02	trans.	M	m			M	tr	m				
OM10-04	trans.	M	m			M			tr			
OM10-05	trans.		tr			M						
OM09-13	s.p.					M			m			
OM09-14	s.p.					M	M				m	
OM10-01	s.p.					M	M				m	
OM10-08	s.p.					M						
OM10-06	s.p.					M	M					
OM10-07	s.p.					M	M		tr			m

^a Type abbrev.: listv. = listvenite, trans. = listvenite-serpentinite transition zone, s.p. = serpentinized peridotite

^b Mineral abbrev.: mgs = magnesite, dol = dolomite, cc = calcite, qtz = quartz, serp = serpentine, ol = olivine

tlc = talc, chl = chlorite, fuchs = fuchsite, en = enstatite, di = diopside

M = major phase, m = minor phase, tr = trace phase.

Table 2

Table 2. Averaged clumped isotope data for listvenites and associated rocks

Sample	Session	Type	Min.	n	$\delta^{13}\text{C}$, ‰ PDB ^a	$\delta^{18}\text{O}_{\text{CO}_2}$, ‰ SMOW ^a	$\delta^{18}\text{O}_{\text{carb}}$, ‰ PDB ^v	$\Delta 47_{\text{ARF}}$, ‰ ^{c,d}	T, °C Bristow ^e
OM09-19	2011	listv.	Dol	1	0.71 ± 0.25	34.22 ± 0.05	-5.73	0.519 ± 0.032	96 + 19 /-
OM09-20-c	2012	listv.	Dol	2	0.99 ± 0.05	33.90 ± 0.07	-6.03	0.511 ± 0.041	101 + 27 /-
OM09-20-f	2012	listv.	Dol	2	0.73 ± 0.03	34.64 ± 0.04	-5.32	0.489 ± 0.024	114 + 17 /-
OM10-14	2012	listv.	Dol	2	-1.75 ± 0.03	28.44 ± 0.04	-11.28	0.555 ± 0.030	78 + 15 /-
OM10-15	2011	listv.	Dol	2	-0.30 ± 0.02	33.43 ± 0.08	-6.48	0.504 ± 0.026	104 + 17 /-
OM10-20	2012	listv.	Dol	2	-0.46 ± 0.05	35.09 ± 0.01	-4.89	0.552 ± 0.039	79 + 20 /-
OM09-11	2012	listv.	Mgs	2	0.62 ± 1.03	32.93 ± 1.13	-7.43	0.521 ± 0.045	95 + 28 /-
OM09-15	2012	listv.	Mgs	2	-2.39 ± 0.34	31.32 ± 0.51	-8.97	0.557 ± 0.029	77 + 14 /-
OM09-16	2012	listv.	Mgs	2	-0.97 ± 0.15	30.96 ± 1.16	-9.32	0.517 ± 0.041	97 + 25 /-
OM09-18	2012	listv.	Mgs	2	-1.61 ± 0.04	31.49 ± 0.11	-8.81	0.514 ± 0.036	99 + 23 /-
OM09-19	2011	listv.	Mgs	2	0.16 ± 0.12	33.86 ± 0.33	-6.53	0.560 ± 0.021	76 + 10 /-
OM10-03	both	listv.	Mgs	3	-2.49 ± 0.15	31.99 ± 0.25	-8.33	0.596 ± 0.019	61 + 8 /-
OM10-26	2011	listv.	Mgs	2	0.09 ± 0.02	34.15 ± 0.10	-6.26	0.530 ± 0.013	90 + 7 /-
OM10-02	2012	trans.	Mgs	1	-0.68 ± 0.04	31.90 ± 0.08	-8.42	0.570 ± 0.054	71 + 26 /-
OM10-04	2012	trans.	Mgs	2	-3.62 ± 0.33	32.42 ± 0.36	-7.91	0.671 ± 0.023	37 + 7 /-
OM11-43	2012	metased.	Cc	1	-2.50 ± 0.04	29.22 ± 0.08	-9.74	0.437 ± 0.065	155 + 84 /-
OM11-45	2012	metased.	Cc	1	-0.17 ± 0.04	30.08 ± 0.08	-8.91	0.442 ± 0.050	150 + 57 /-
OM11-48	2012	metased.	Cc	1	-0.57 ± 0.04	28.99 ± 0.08	-9.96	0.421 ± 0.063	171 + 96 /-
OM11-47	2012	metased.	Dol	1	-4.53 ± 0.04	30.39 ± 0.08	-9.41	0.588 ± 0.059	64 + 27 /-

^a For n≥2, uncertainty is one standard deviation of replicate digestions (which exceeds internal error). For n=1, reported uncertainty is the greater of the internal standard deviation of all sample acquisitions or the session standard deviation of calcite standards relative to expected value.

^b Carbonate $\delta^{18}\text{O}$ values calculated from phosphoric acid digestion fractionation factors at 90°C (Das Sharma et al., 2002)

^c clumped data converted from Caltech reference frame to absolute reference frame of Dennis et al. (2011) using a transfer function derived from calcite standards and heated gases analyzed during both analytical session. See Supplementary Table S3.

^d Reported uncertainty is the propagated internal standard deviation over all acquisitions of each digestion (which exceeds the standard deviation of replicate digestion though typically similar in magnitude);

^e Temperature calculated using the calcite- and dolomite-derived calibration implied by the data of Bristow et al. (2011), converted to the absolute reference frame: $\Delta 47 = 0.0012x^2 + 0.0285x + 0.245$, where $x = 10^6/T^2$. For T derived from other calibrations, see Supplementary Table S2, which includes all clumped isotope data (samples, known-T mgs, stds, HG).

^f Reported uncertainty is the 1-stdev uncertainty of $\Delta 47_{\text{ARF}}$, propagated through the temperature calculation

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Figure 13