# Geochemical and C-O isotopic study of ophiolite-altered carbonates of the Barzaman Formation, Oman: Evidence of natural CO2 sequestration via carbonation of ultramafic clasts

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#### Abstract

Carbonate mineral precipitation via capture of atmospheric  $CO_2$  by alkaline-hyperalkaline waters offers a potential strategyreferred to as carbon capture and storage-to mitigate anthropogenic  $CO_2$  emissions. Oman ophiolite produces high-pH waters characterized by continuous sequestration of atmospheric  $CO_2$ . The geochemical and isotopic data of carbonates are utilized to assess the  $CO_2$  stored in dolomite-calcite assemblage of the Barzaman Formation. PAAS-normalized REE+Y patterns display increasing LREE, flat HREE, and a positive Eu-anomaly, identical to those of the bulk ocean crust and lower crust. Further, La(+), Ce(-), and Y(+) anomalies in studied samples are missing in the ocean crust, however, present in local groundwater and modern seawater. Carbon and oxygen isotopes show two distinct end-members, heavier dolomite than calcite. The estimated carbonate growth temperatures (18 to 65) are indistinguishable from literature values. The C-O isotope model of dolomitecalcite assemblage, water, and atmospheric  $CO_2$  demonstrates that the C-budget of ophiolite-derived carbonates represent an unequivocal contribution from the latter. Meanwhile, the remaining contributors may include dissolved inorganic carbon (DIC) in waters closely associated with travertines and ophiolite-derived soil exhibiting large variations in their C-O isotope compositions caused by kinetic fractionation leading to isotopic disequilibrium. Taken together, REE+Y patterns and isotopic compositions verify that the carbonates were formed under oxic conditions through alterations triggered by the reaction between ophiolite and meteoric water. A detailed groundwater study is recommended to assess the contribution of atmospheric  $CO_2$  in DIC for a thorough estimation of the amount of  $CO_2$  sequestered by carbonates of the Barzaman Formation.

# Key Points

- 1. First geochemical and isotopic datasets of carbonate rocks from the Barzaman Formation, Oman
- 2. Carbon and oxygen isotopic model to determine the contribution of atmospheric CO<sub>2</sub> deposited by carbonates via carbonation of ultramafic clasts
- 3. Estimation of growth temperatures of carbonate rocks, calculated from their isotopic compositions

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14	hyperalkaline waters offers a potential strategy-referred to as carbon capture and storage-
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17	isotopic data of carbonates are utilized to assess the CO2 stored in dolomite-calcite
18	assemblage of the Barzaman Formation. PAAS-normalized REE+Y patterns display
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20	ocean crust and lower crust. Further, La(+), Ce(-), and Y(+) anomalies in studied samples
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23	The estimated carbonate growth temperatures (18°C to 65°C) are indistinguishable from
24	literature values. The C-O isotope model of dolomite-calcite assemblage, water, and
25	atmospheric CO2 demonstrates that the C-budget of ophiolite-derived carbonates represent
26	an unequivocal contribution from the latter. Meanwhile, the remaining contributors may
27	include dissolved inorganic carbon (DIC) in waters closely associated with travertines and
28	ophiolite-derived soil exhibiting large variations in their C-O isotope compositions caused
29	by kinetic fractionation leading to isotopic disequilibrium. Taken together, REE+Y patterns
30	and isotopic compositions verify that the carbonates were formed under oxic conditions
31	through alterations triggered by the reaction between ophiolite and meteoric water. A
32	detailed groundwater study is recommended to assess the contribution of atmospheric CO <sub>2</sub> in

33 DIC for a thorough estimation of the amount of CO<sub>2</sub> sequestered by carbonates of the

34 Barzaman Formation.

*Keywords:* C-O isotopes, Carbonates, Barzaman Formation, Alteration, CO<sub>2</sub>
 Sequestration, Oman Ophiolite

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38 **Plain Language Summary** The sequestration of CO<sub>2</sub> by mineralization is the subject of 39 much debate and one of the potential methods for dealing with the increasing levels of 40 anthropogenic CO<sub>2</sub> emissions. We analyzed the carbonate rocks from the Barzaman 41 Formation in Oman for their geochemical and isotopic compositions to assess the 42 contribution of atmospheric CO<sub>2</sub> stored in them. Geochemical signatures of these samples 43 indicate that they are closely related to the oceanic crust, a precursor of Oman Ophiolite. 44 Our estimate, based on the carbon and oxygen isotope system, suggests that a certain 45 amount of the total carbon budget of carbonate samples comes from the atmospheric CO<sub>2</sub>. 46 The other half, however, may reflect the dissolved inorganic carbon (DIC) in waters produced by the interaction with the travertines and soil formed earlier. Significant amounts 47 48 of atmospheric  $CO_2$  may be stored in the DIC species, but the overall estimation requires 49 further specific groundwater investigations.

50

#### 51 **1. Introduction**

52 Water plays a pivotal role in Earth's surface to subsurface conditions in geological

53 processes at low-temperature temperatures (< 60°C) such as, serpentinization, diagenesis,

and alteration of ultramafic rocks (Müller et al., 1972; Neal & Stanger, 1984, 1985; Clark

55 & Fontes, 1990; Neal and Shand, 2002; Schlüter et al., 2008; Kelemen et al., 2011;

56 Kelemen and Hirth, 2012; Streit et al., 2012; Schrenk et al., 2013; Lacinska et al., 2014;

57 Miller et al., 2016; De Obeso & Kelemen, 2018; Giampouras et al., 2019, 2020). Oman

58 ophiolite exhibits active interactions between water and rock in the subaerial

59 environments. Due to the growing interest in carbon capture and storage (CCS) to

60 eradicate climate change (Meinshausen et al., 2009), several studies on hyperalkaline

61 waters and mineral precipitations, resulting from water pools, have recently been

62 conducted to understand the reaction mechanism and kinetics of natural CO<sub>2</sub>

63 sequestration (Seifritz, 1990; Kelemen & Matter, 2008; Matter & Keleman, 2009;

64 Kelemen et al., 2011; Streit et al., 2012; Paukert et al., 2012; Giampouras et al., 2020).

65 Moreover, various carbonate materials directly linked to ophiolites (e.g., travertines, 66 magnesite and calcite veins, breccia, conglomerates, limestones, listwanites) from Oman 67 and the neighboring United Arab Emirates (UAE) have also been investigated to better 68 constraint the natural CO<sub>2</sub> fixation (Nasir et al., 2007; Kelemen & Matter, 2008; Kelemen 69 et al., 2011; Paukert et al., 2012; Stephen et al., 2013; Stephen, 2014; Lacinska et al., 70 2014). Ophiolite-derived clasts dominate the conglomerates of the Barzaman Formation 71 (11.6 to 3Ma, late Miocene – Pliocene; Salad Hersi et al., 2013) with no metamorphic 72 rock clasts (Jacobs et al., 2015). In a recent study, based on the field observations, it has 73 been suggested that ophiolite-derived Barzaman Formation conglomerates from the UAE 74 stored significant amounts of CO<sub>2</sub> (~150 billion tonnes, i.e., 4 years of global emissions 75 at current rates) through extensive alteration of ophiolite to carbonated rocks (Lacinska et 76 al., 2014). Due to the silica-carbonate conversion, the chemical alteration of the ophiolite 77 clasts into dolomite-calcite assemblage has been facilitated by water circulation in the 78 presence of atmospheric  $CO_2$  under near-surface conditions. For  $CO_2$  fixation, the 79 chemical reaction of the ophiolite, water, and CO<sub>2</sub> to produce dolomite-calcite 80 assemblage is essential to reduce the ever-increasing CO<sub>2</sub> in the atmosphere and act as an 81 analogue for CO<sub>2</sub> sequestration in ophiolite. We conducted field observations and 82 laboratory measurements of carbonate rocks exposed at Sultan Qaboos University 83 campus and nearby Wadi Al Khod to understand the process of chemical alteration of 84 ophiolite clasts to the dolomite-calcite assemblage (Figures 1, 2). 85 Water reaction with Mg- and Ca-bearing minerals in ultramafic rocks in the fractured Oman 86 ophiolite provides an opportunity for spontaneous binding of CO<sub>2</sub> either from dissolved species in water (e.g., dissolved inorganic carbon (DIC) =  $H_2CO_3$ ,  $HCO_3^-$ ,  $^2CO_3^{2-}$ ) or from 87 88 atmospheric CO<sub>2</sub>. Our motivation is to study the geochemical and stable isotope 89 characteristics of carbonate rocks of the ophiolite alteration origin (e.g., carbonated 90 conglomerates) from the Barzaman Formation, Oman. In this study, we analyzed the 91 massive dolomite-calcite horizons, and altered ophiolite clasts and matrix within the 92 Barzaman Formation to understand the atmospheric CO<sub>2</sub> absorption during chemical 93 alteration of the ophiolite clasts into the carbonate rocks. 94

### 95 2. Geological Background

96 The study area is covered mostly by the rocks of the Barzaman Formation and the Samail 97 ophiolite (Béchennec et al., 1992) (Figure 1a). The exposed ophiolitic rocks are comprised 98 of serpentized and carbonatized harzburgite, dunite, layered gabbro, sheeted dykes and 99 pillow lava. Spectacular examples of carbonation of harzburgite and dunite rocks in Oman 100 were presented by Kelemen and Matter (2008) and Matter and Kelemen, (2009). In the 101 Samail ophiolite, complex interactions between surface fluids, mantle peridotites and CO<sub>2</sub> 102 have generated large-scale, superficial and deeper carbonate deposits of relevant extension 103 through time, together with actively forming deposits (Matter & Kelemen, 2009). The 104 Barzaman Formation of late Miocene to Pliocene age is exposed in the Al Khod area as 105 isolated outcrops consisting of conglomerate, sandstone, mudstone, and carbonate rocks 106 (Figures1b-c). The conglomerate and sandstone comprise clasts derived from the Samail 107 Ophiolite, commonly referred to as Oman Ophiolite, and Hawasina sequences. The 108 conglomerate clasts are largely comprised of dunite, peridotite and gabbro, which are 109 susceptible to chemical alteration under surface and near-surface conditions, whereas, red 110 and green chert from the Hawasina sequence is inert (Figures 2a-b). There are two types of 111 carbonates in the Barzaman Formation, a fossiliferous limestone deposited as small patch 112 reefs, and dolomite that formed due to post-depositional chemical alteration of the ophiolite 113 clasts (Figure 1c, Figure 2a-g). The diagenetically-produced carbonates of the Barzaman 114 Formation are termed as Barzamanite (Maizels, 1987) and constitute an important 115 component of the Barzaman Formation in its type locality, as well as those in Wadi Al 116 Khod, parts of the SQU campus (Figures 1a-b; Figure 2a-b) and parts of the Bataina coast. 117 The carbonates of the Barzaman Formation are pinkish-white, massive, and dense 118 containing abundant chert clasts (Figures 2d-f). Within the massive dolomite and calcite, 119 occasional unaltered peridotite clasts are also present (Figure 2f). The studied outcrops have 120 undergone different degrees of ophiolite clast alteration during diagenesis showing ghost 121 textures of the primary clasts relicts (Figure 2g).

122 **3. Materials and Methods** 

123 **3.1. Samples** 

124 A suite of carbonate samples selected for the present study is listed in Table 1, providing

125 their location coordinates and mineralogical details. Half of the samples were collected from

126 the Sultan Qaboos University (SQU) campus and consist mainly of the dolomite-calcite

- 127 assemblage with quartz and halite as minor phases, including two samples of fossiliferous
- 128 limestone. The remaining samples were collected from nearby Wadi Al Khod, and are

identical in mineralogy to the samples from the SQU (Figure 1b).

130

### 131 **3.2.** X-ray Diffractometry (XRD) and Scanning Electron Microscopy (SEM)

132 X-ray powder diffraction analyses for phase identification were done with a MiniFlex600

- 133 XRD (Rigaku) at Earth Sciences Research Centre (ESRC). Samples were finely pulverized
- 134 with agate mortar and pestle before preparing block samples on an aluminum sample plate
- 135 for exposure to Cu K $\alpha$  radiation (40kV and 15mA) with a scanning speed of 2.5° 2 $\theta$ min<sup>-1</sup>.
- 136 Using PDXL qualitative analysis software combined with a licensed database (PDF-4

137 Minerals 2020 RDB) provided by the International Centre for Diffraction Data (ICDD<sup>®</sup>), the

138 data obtained were processed for peak identification–including position, height, integrated

- 139 intensity, and full width at half maximum (FWHM).
- 140 The sample was mounted onto a standard aluminum SEM stub using carbon paint and
- 141 coated with thin platinum film for having images of surface morphologies using Field
- 142 Emission SEM (JEOL JSM-7600, Japan) facility at the Central Analytical and Applied

143 Research Unit (CAARU) of SQU.

144

#### 145 **3.3. ICP-OES and ICP-MS**

- 146 Inductively coupled plasma spectrometry was utilized for measuring the concentrations of
- 147 major, minor and trace elements including rare earth elements (REE). Powdered samples
- 148 were digested with HCl, HF, and HNO3 suprapur acids Merck as described in Nogueira et
- al. (2019). Major and minor elements were analyzed using Agilent 725 ICP-OES, and trace
- and REE were measured with Agilent 770 ICP-MS, both housed at the Geochemistry
- 151 Laboratory (LGQa) of the Federal University of Ouro Preto, Brazil. To monitor the
- 152 instrumental performance, reference material BRP1 (Basalto Ribeirão Preto) was analyzed
- 153 intermittently. The percent deviations of obtained data from those of the certified values of
- 154 BRP1 range from  $\pm 0.5\%$  for 28 elements and  $\pm 6.10\%$  for six elements.
- 155

#### 156 **3.4. Carbon and Oxygen Isotope Measurements**

157 Stable C and O isotope compositions were measured at the LGQa of the Federal

- 158 University of Ouro Preto, Brazil. The isotopic compositions of carbon and oxygen were
- 159 obrained for all the samples by a closed tube reaction with orthophosphoric acid (100%)
- 160 at 72°C using a Thermo Finnigan Delta V advance Mass Spectrometer coupled with
- 161 GasBench II. The average values obtained for the standards NBS-18 (7.20%; Coplen,
- 162 1996), NBS-19 (28.60%; Coplen, 1996); and LSCEC (-46.60%; Coplen et al., 2006),
- 163 NBS-19 (1.95‰; Coplen et al., 2006) were used to normalized the raw data in each run to
- 164 the VSMOW and VPDB scale respectively. The C-O isotope ratios are expressed in  $\delta$
- 165 notation as  $\delta^{13}$ CvPDB and  $\delta^{18}$ OvSMOW following corrections relative to Vienna Pee Dee
- 166 Belemnite (VPDB) and Vienna Standard Mean Ocean Water (VSMOW), respectively.
- 167 Measured values of standard samples (NBS-18, NBS-19, LSVEC) suggest that the
- analytical accuracy is better than  $\pm 0.1\%$  (Nogueira et al., 2019).
- 169

### 170 **4. Results and Discussions**

#### 171 **4.1. Geochemical Features**

172 XRD patterns of our samples show that they consist mainly of carbonate minerals (e.g., 173 dolomite-calcite assemblage) with minor phases, including quartz and halite (Figs. 3a, 3c). 174 In addition to the dolomite-calcite assemblage crystal lattices, several fibrous materials are 175 also found in the FE-SEM images (Figs. 3b, 3d). Quantitative measurements of major 176 elements indicate that the samples stoichiometrically reflected dolomite-calcite 177 compositions (Table 2), supporting the qualitative data (Figure 3).

178 PAAS-normalized REE patterns of all the samples exhibit La-Sm depletions in light-REE

179 (LREE; La-Sm) relative to heavy-REE (HREE; Eu-Lu) and nearly flat trends in HREE.

180 Weak to moderate negative Ce-anomalies (-0.05 to -0.48) look pronounced due to the

181 positive La-anomalies (Figure 4). Furthermore, most of the studied samples also show

- 182 positive Eu- and Y-anomalies. The REE values are well below the PAAS values (i.e.,
- 183 ranging between 0.01 to 0.3 in different elements), which confirm that carbonate rocks
- 184 generally contain lower REE content than shales (Tobia, 2018). For comparison, the PAAS-
- 185 normalized REE values of the entities are plotted that are closely related to the studied
- 186 samples (Figure 4), including Oman ophiolite, bulk oceanic crust, lower crust, seawater
- 187 (Pacific), and groundwater (Al Khod area, Oman). Some of the observations made from this

188 comparison include: i) patterns of the samples analyzed in this study suggest that they all are 189 identical, including the fossiliferous limestone that underlie the Barzaman Formation (i.e., 190 Bl.S1 and Bl.S2), ii) incomplete Oman ophiolite pattern is also nearly identical to the 191 studied samples with two- to tenfold enrichment in Sm to Lu compared to that of the PAAS, 192 iii) the trends in all samples mimic the patterns shown by bulk ocean crust and the lower 193 crust characterised by Eu-anomaly except La (positive), Ce (negative) and Y (positive). 194 However, La-, Ce- and Y-anomalies are similar to those of the groundwater (Al Khod, 195 Oman; Semhi et al., 2009) and seawater (South Pacific seawater at a depth of 2m; Zhang & 196 Nozaki, 1996), iv) most of the samples indicate weak Ce-anomaly (-0.05 to -0.48) that 197 apparently look stronger because of the positive La-anomaly. The total REEs of the studied 198 samples vary from 5-19 ppm with the lowest value observed in fossiliferous limestone and 199 the highest in dolomite. The higher value in dolomite is slightly below the typical marine 200 carbonates (i.e., ~28 ppm; Bellanca et al., 1997). Similarly, the sum of REE +Y ranges from 201 6.5 to 25.5 ppm, following the same trend in Y concentration as observed in total REEs.

202

#### 203 4.1.1. Ce- and Eu-anomaly

204 Depletion of Ce relative to neighboring REEs (German & Elderfield, 1990; Morad & 205 Felitsyn, 2001) is an important feature of the groundwater (Semhi et al., 2009) and modern seawater (Zhang & Nozaki, 1996) resulting from oxidation of Ce<sup>3+</sup> to the less soluble Ce<sup>4+</sup> 206 207 which is easily scavenged by the suspended particles (Nogueira et al., 2017). The Ce/Ce\* 208 values (Bau & Dulski, 1996) of the analyzed samples, including fossiliferous limestone, 209 ranging from 0.65 to 0.96 except for two samples (Kd8 = 0.36 and Bl.S2 = 0.52) and are 210 higher than the typical Ce/Ce\* range in seawater (<0.1 to 0.4), which is likely to indicate oxygenated precipitating conditions. The reduction of Eu<sup>3+</sup> into Eu<sup>2+</sup> state under low 211 oxidation and neutral pH conditions produces Eu<sup>2+</sup> ion-rich pore waters compared to 212 neighboring REE<sup>3+</sup>. However, when high oxidation conditions are available, Eu is 213 incorporated into the precipitating materials as  $Eu^{3+}$  (Stipp et al., 2003), thus producing a 214 215 positive Eu-anomaly.

216

#### 217 **4.1.2. La-anomaly**

- 218 To evaluate the possible effects on Ce-anomaly (referred to as Ce<sup>\*</sup> in the text) caused by 219 anomalous enrichment of La in our samples, the Ce/Ce\* and Pr/Pr\* (Bau & Dulski, 1996) 220 values are calculated which are ranging from 0.53 to 0.96 and 0.96 to 1.25, respectively. To 221 distinguish between La and Ce anomalies, a plot of Pr/Pr\* vs. Ce/Ce\* can be divided into six 222 different fields (Figure 5a). Most of the samples fall into a positive La-anomaly field that 223 causes weaker Ce anomalies to look substantially stronger except for five samples that fall 224 solely into the negative Ce-anomaly field (Figure 5a). This implies that a pseudo-Ce-225 anomaly induced by the positive La-anomaly (Ce/Ce\* > 0.7; Pr/Pr\* < 1.05) may be 226 represented by  $Ce_*^* > -0.2$  (Figure 5a). When  $Ce/Ce^*$  and  $Pr/Pr^*$  ratios (Bau & Dulski, 1996) are plotted against Ce<sup>\*</sup>, linear regressions with respectively opposite slopes of -0.66 and 227 228 +1.41 are observed (Figure 5b). Both lines intersect at  $Ce_*^* = +0.02$ , which implies that real negative Ce-anomaly is prominent as the difference between Pr/Pr\* and Ce/Ce\* ratios 229 230 increases and vice versa (Figure 5b). It also suggests that the studied samples might have 231 been precipitated under varying oxidation conditions; in particular, two dolomite samples 232 (e.g., Kd1 and Kd8) encountered a highly oxic environment.
- 233

#### **4.1.3. Y-anomaly**

235 Most of the studied samples show a weak Y-anomaly compared to that of seawater (Figure 236 4). Stronger ionic complexation and hence longer residence time of yttrium in seawater is 237 responsible for strong positive Y-anomaly compared to its weak covalent sorption on the 238 particulate matter. The geochemical properties of yttrium are similar to those of HREEs, 239 especially with Ho, and yttrium is often referred to as a pseudo-lanthanide. Therefore, Y-240 anomaly can be evaluated by the Y/Ho ratio that is almost constant in all terrestrial rocks 241 (i.e., ~ 26; Bolhar et al., 2004). However, our data shows a range (from 6 to 21, Table 2) that 242 is lower than the value of 26 for terrestrial rocks and 200 for seawater. The apparent 243 difference may be linked to the type of water from which carbonates precipitated. For 244 example, water which offers more ionic complexation sites will produce a higher Y/Ho ratio 245 and vice versa.

246

#### 247 **4.1.4. Ni-Cr-V Mobility**

248 Because of the mobile nature of the Ni, Cr, and V, the distribution of these heavy metals in 249 the studied samples is evaluated and compared with those in groundwater, oceanic crust, and 250 MORB. The mobility order Ni > Cr > V determined in mineral horizons (Agnieszka & Barbara, 2012) is in contrast to the ionic radii (i.e.,  $Ni^{2+} = 83$  pm  $Cr^{2+} = 87$  pm,  $V^{2+} = 93$  pm; 251 252 Shannon, 1976). We noticed a non-linear mixing trend between groundwater and ultramafic 253 rocks by plotting Cr/Ni and Ni/V ratios (Figure 6), which may have implications for the 254 duration of water-rock interaction. Longer duration of fluid-rock interaction increases Ni 255 content in water, causing a decrease in Cr/Ni and an increase in Ni/V ratio. This means that alkaline and hyperalkaline waters with varying amounts of  $Mg^{2+}$  (86 pm) and  $Ca^{2+}$  (114 pm) 256 can, because of their relatively smaller ionic sizes, enable heavy metal ions to bind to their 257 258 aqueous species (e.g.,  $Mg^{2+}$ -HCO<sub>3</sub><sup>-</sup> and Ca<sup>2+</sup>-OH<sup>-</sup>). The heavy metal signatures of these waters would subsequently be fingerprinted on carbonates formed by reaction with 259 260 atmospheric CO<sub>2</sub>.

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262

#### 4.2. **Carbon and Oxygen Isotope Signatures**

The compositions of stable carbon and oxygen isotopes (i.e.,  $\delta^{13}$ C<sub>VPDB</sub> and  $\delta^{18}$ O<sub>VSMOW</sub>; 263 264 Table 3) of carbonate samples vary from -7.8‰ to -9.9‰ and +21.4‰ to +27.3‰, 265 spanning over the range of  $\sim 2\%$  and  $\sim 6\%$ , respectively (Figure 7). By plotting these 266 values with previously reported data (Figure 7), we noticed an extension in the trend laid 267 out by the mean values of conglomerates, breccia, magnesite, and calcite veins (Kelemen 268 et al., 2011, Stephen et al., 2013, Stephen, 2014). Most of our data falls within the 269 isotopic equilibrium area suggested by Falk et al. (2016). In the present study, dolomite 270 samples (e.g., CC2 = -7.8%, +27.3% and CC3 = -8%, +26.9%) show comparatively 271 heavier isotope compositions than those of the calcite (e.g., OC9 = -9.9%, +21.5% and OC10 = -9.1‰, +22.9‰). The observed enrichment of  $\delta^{18}$ Ovsmow (~5‰) in dolomite 272 273 relative to calcite is supported by the observation made by O'Neil and Epstein (1996) for the dolomite-calcite assemblage at ambient temperature (i.e., 25° C; ~6.8‰). Assuming 274 275 dolomite-calcite assemblage as two end-members, the remaining samples with variable 276 mineralogy fall down on a mixing line with a slope of 1/3 (Figure 7). Furthermore, the dolomite end-member shows a value of  $\delta^{18}O_{VSMOW}$  (i.e., ~27‰), similar to that of the 277 278 calculated CaCO<sub>3</sub> precipitating in isotopic equilibrium from groundwater (pH = 7-8) and

279atmospheric CO2. Meanwhile, calcite end-member falls close to the expected  $\delta^{13}C_{VPDB}$ 280composition of CaCO3 precipitating in equilibrium with groundwater (see blue-dotted

- 282 In order to estimate the  $\delta^{13}$ CVPDB and  $\delta^{18}$ OVSMOW compositions of CaCO<sub>3</sub> formed in
- equilibrium from  $Ca^{2+}$  cations in water and ambient  $CO_2$ , the mean oxygen isotope values
- of different types of water are used, such as, ophiolite-derived water (pH >10,  $\delta^{18}$ Ovsmow
- 285 = -1.35‰), limestone-derived water (pH = 7-8,  $\delta^{18}$ Ovsmow = -3.2‰), limestone aquifer
- 286 water (pH = 7-8,  $\delta^{18}$ Ovsmow = -2.55‰), alkaline water (pH >8<11,  $\delta^{18}$ Ovsmow = -
- 287 0.05‰), hyperalkaline water (pH>11,  $\delta^{18}$ Ovsmow = -1.3‰), and seawater (pH =7.5-8.4,
- 288  $\delta^{18}$ Ovsmow = 0‰) reported elsewhere (Stephen, 2014). Using the equation (1) given by
- 289 Clark et al. (1992), the calculated  $\delta^{18}$ O<sub>CaCO3-VSMOW</sub> values for the precipitating CaCO<sub>3</sub>
- 290 vary within a small range (e.g., 26.4% to 27.5%; mean = 27%).

291 
$$\delta^{18}O_{CaCO_3} = \frac{1}{3}\delta^{18}O_{H_2O} + \frac{2}{3}\cdot\delta^{18}O_{CO_{2(g)}}, \qquad (1)$$

292 The  $\delta^{13}$ CVPDB values of the CaCO<sub>3</sub> are calculated using the equation of Deines et al.

- 293 (1974) for temperature ranging from 0 to 45° C (Stephen, 2014).
- 294

281

line in Figure 7).

$$\delta^{13}C_{(CaCO_{3}(eq))} = \delta^{13}C_{CO_{2}(g)} - \epsilon^{13}C_{CO_{2}(g)} - CaCO_{3},$$
(2)

295 Where  $\epsilon$  represents the fractionation factor between CO<sub>2</sub> and CaCO<sub>3</sub>. The estimated  $\delta^{13}C_{CaCO3-VPDB}$  decreases from +5.4‰ to +1.2‰ with the increase of temperature from 0 296 to 45° C (Figure 7). Hyperalkaline waters contain carbon contents that are too low to be 297 298 analyzed for isotopic measurements given their high pH values that provide an efficient reaction opportunity between  $Ca^{2+}$  in the water and atmospheric CO<sub>2</sub>. However, carbon 299 isotope compositions of dissolved inorganic carbon (i.e.,  $\delta^{13}C_{DIC}$ ) in low pH waters are 300 301 variable, such as surface alkaline ophiolite-aquifer water (-26.8 to -6.6%; Stephen, 2014) 302 and limestone aquifer water (-8.7 to -3.9%; Stephen, 2014). Groundwaters from Al Khod 303 area, with pH values around 7.3-8.5 (Semhi et al., 2009), can contain DIC species from 304 various sources, including soil CO2 and dissolved carbonate minerals (Deines et al., 305 1974).  $\delta^{13}C_{\text{soil-DIC}}$  for Oman ophiolite has been reported as low as -23‰ by Clark (1987). 306 In order to approximate the isotopic composition of groundwater from Al Khod area, we 307 assumed that both soil  $CO_2$  and dissolved carbonate minerals contribute equally (i.e., 1:1) 308 ratio; Stephen, 2014) towards chemical and isotopic equilibrium of groundwater. For

example,  $\delta^{13}$ CVPDB of groundwater is estimated to be -10.9‰ using  $\delta^{13}$ Cgroundwater =  $\frac{1}{2}$  \* 309 310  $(\delta^{13}C_{\text{soil-CO2}} + \delta^{13}C_{\text{dissolved mineral}})$  for  $\delta^{13}C_{\text{soil-CO2}} = -23\%$  (reported as  $\delta^{13}C_{\text{soil-DIC}}$ ; Clark, 1987) and  $\delta^{13}C_{dissolved mineral} = +1.2\%$  calculated for the calcite precipitating in equilibrium 311 with water at an ambient temperature of 45°C (Figure 7). Previously reported  $\delta^{13}$ CVPDB 312 313 values of waters from sedimentary aquifers (i.e., limestone and dolomite dominated 314 environments) and limestone-aquifers across Oman range from -6.2 to -8.5‰ (Matter et al., 2006) and -3.9 to -8.5% (Stephen, 2014), respectively. The studied dolomite samples 315 316 (e.g., CC2 and CC3) represent  $\delta^{13}$ CVPDB values (-7.8 to -8.0‰) fairly close to the atmospheric CO<sub>2</sub> value (-7‰), and both values are falling in the isotopic equilibrium box 317 318 (Falk et al. 2016). However, the estimated  $\delta^{13}C_{VPDB}$  value of carbonate (+1.2‰ at 45°C) 319 precipitating in equilibrium from water and atmospheric  $CO_2$  is higher than that of the 320 latter (-7‰). In contrast, the  $\delta^{13}$ C<sub>VPDB</sub> of our calcite sample (OC9 = -9.9‰) is close to the 321 value of the carbonate (-10.9‰) precipitating in equilibrium from the groundwater of Al 322 Khod area and atmospheric CO<sub>2</sub>. The discrepancy in estimated  $\delta^{13}$ C<sub>VPDB</sub> of isotopically 323 equilibrated precipitating carbonate and the actual dolomite samples suggest that the 324 latter contain a mixture of carbon sources, such as, DIC in groundwater (i.e., ophiolite 325 soil CO<sub>2</sub> and dissolved limestone CO<sub>2</sub>) and atmospheric CO<sub>2</sub>. The concentrations of 326 dissolved carbonates and bicarbonates in water are predominantly higher at pH > 7327 compared to at pH < 7 (Zeebe, 1999) because of the aqueous CO<sub>2</sub> reactions (e.g., 328 hydration and hydroxylation; Boettger, 2017). Hyperakaline waters (pH>11) rapidly 329 capture atmospheric CO<sub>2</sub> to form bicarbonates via hydroxylation reaction (Boettger, 330 2017) and subsequently precipitate into insoluble carbonates showing isotopic disequilibrium – caused by kinetic fractionation – and very low  $\delta^{13}$ CVPDB as seen in 331 332 travertines (Figure 7). Our data suggest that carbonates from Barzaman Formation may 333 have been formed in isotopic equilibrium with meteoric water – having the previous 334 carbon-budget as DIC species derived from ophiolite soil and previously formed 335 carbonates (e.g., travertines) – and atmospheric CO<sub>2</sub>. It is estimated that the contribution 336 of carbon in the dolomite-calcite assemblage of the Barzaman Formation is equally 337 derived from the CO<sub>2</sub> in DIC and atmosphere. Contributions of atmospheric CO<sub>2</sub> in the 338 DIC portion would be required to estimate the actual amounts of atmospheric CO<sub>2</sub> 339 sequestered by the carbonates from the Barzaman Formation. We recommend further

340 studies on <sup>14</sup>C-dead carbon estimation and clumped isotope measurements in order to

341 calculate the actual contribution of atmospheric CO<sub>2</sub> in the Barzaman Formation

342 carbonates.

343

#### 344 **4.3.** Carbonate Formation Temperature Estimation

Using O'Neil et al.'s (1969) equation, later revised by Hays and Grossman (1991) as
equation (3) below, the formation temperatures (18°C to 65°C) of the studied samples are
calculated, which are in agreement with the previously estimated temperature range
determined by CO<sub>2</sub> clumped isotope thermometry in carbonates from Oman (18°C to 66°C;
De Obeso & Kelemen 2018; Kelemen et al., 2011).

350

$$T_{(^{\circ}C)} = 15.7 - 4.36 (\delta^{18}O_{VPDB(calcite)} - \delta^{18}O_{VPDB(calcite)})$$

351  $\delta^{18}O_{VSMOW(water)} + 0.12 \left(\delta^{18}O_{VPDB(calcite)} - \delta^{18}O_{VSMOW(water)}\right)^2, \quad (3)$ 

For this purpose, the  $\delta^{18}$ vsmow values of different water types, such as, limestone-aquifer 352 353 (LAW), limestone-derived (LDW), ophiolite-derived (ODW), hyperalkaline (HAW), 354 alkaline (AW), and seawater (SW) (Stephen, 2014) and  $\delta^{18}$ <sub>VPDB</sub> of carbonates (this study) are used (Figure 8). Temperature ranges for dolomite and calcite are 18°C to 33°C and 46°C 355 356 to 65°C, respectively, when LDW and AW compositions are used. Dolomite samples show 357 comparatively lower formation temperatures than those of the calcite samples with a 358 difference of approximately 30°C (Figure 8). Given the isotopic compositions and estimated 359 temperatures of our samples, we infer that calcite (OC9) precipitated at relatively higher temperatures (46°C to 65°C) with lower  $\delta^{13}$ C<sub>VPDB</sub> compositions (-9.9‰) relative to 360 dolomites (CC2 and CC3; 18°C to 33°C;  $\delta^{13}C_{VPDB} = -7.8\%$  to -8.0%). The fact that the 361 362 isotopic data of the calcite sample (OC9) falls slightly outside the isotopic equilibrium box 363 (Falk et al., 2016) compared to that of dolomite, further suggesting that carbonates of the 364 Barzaman Formation have attained the complete isotopic equilibrium with a decrease in 365 temperature (Figure 7).  $\delta^{18}$ O fractionation between a dolomite-calcite assemblage (5.7‰) 366 closely resembles that of the equilibrium value of 6.8‰ at 25°C reported earlier by O'Neil 367 and Epstein (1966), suggesting that the subtle difference is probably associated with low 368 temperature in the latter case. Alternatively, if dolomite and calcite were formed in isotopic 369 equilibrium then dolomite-calcite  $\delta^{18}$ O fractionation calculated from CO<sub>2</sub>-dol (41.2 - 27.1 =

370	14.1‰) and CO <sub>2</sub> -cal (41.2 – 21.5 = 19.7‰) would be 5.6‰ (O'Neil & Epstein, 1966),
371	which is in excellent agreement with our data (5.7‰).
372	
373	5. Summary and Conclusions
374	The following conclusions have been drawn from the geochemical and isotopic data
375	obtained from the Barzaman carbonates:
376	(1) PAAS-normalized REE + Y patterns are characterized by increasing LREE, flat
377	HREE and Eu-anomaly, identical to those of the oceanic crust except the absence of
378	positive La, negative Ce, and positive anomalies in the latter.
379	(2) Ce, La, and Y anomalies in carbonate samples are characterized by the local Al
380	Khod groundwater and seawater.
381	(3) Carbon and oxygen isotope compositions show isotopically distinct end-member
382	compositions as dolomite-calcite assemblage exhibits comparatively heavier
383	dolomite than the calcite.
384	(4) Stable isotope thermometry provided growth temperatures ranging from 18°C to
385	65°C are in excellent agreement with previously reported values.
386	(5) Modeling of carbon and oxygen isotope system suggests an unequivocal contribution
387	from the atmospheric CO <sub>2</sub> in Barzaman carbonates. The remaining contributors may
388	account for the DIC originated from travertines and ophiolite-derived soil.
389	(6) Taken together, REE + Y distribution patterns and isotopic compositions indicate
390	that the carbonate rocks (dolomite) were formed in an oxic environment by water-
391	induced alteration of the ultramafic rocks belonging to the Oman Ophiolite.
392	(7) For a complete evaluation of the amount of atmospheric CO <sub>2</sub> stored in the Barzaman
393	carbonates, we recommend a detailed groundwater analysis aimed at breaking down
394	the atmospheric CO <sub>2</sub> contribution in DIC.
395	
396	
397	
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- 408

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- 590 Figure 1a. Geological map of the Oman Mountains. The study area is shown in rectangle,
- 591 (modified after Abbasi et al., 2014).



593 Figure 1b. Google map showing sample locations.



Figure 1c. Vertical sections through the Barzaman Formation; a) vertical section of the exposed part of the Barzaman Formation in the CoC parking and adjacent area in the Sultan Qaboos University (SQU). The conglomerate/boulder beds are comprised of the ophiolite and chert clasts. The ophiolite clasts are chemically altered to dolomite, b) the Barzaman Formation in Wadi Al Khod. Most of the Barzaman Formation in the Wadi Al Khod is covered by the wadi scree, whereas only the Barzamanite part is exposed.



625 Figure 2. Field photos of the Barzamanite, (a) Field view of the massive dolomite 626 (Barzamanite) of the Barzaman Formation in Wadi Al Khod. The dolomite unite is about 627 8 m thick dipping 0-5°, and exposed over a large area in the Old Al Khod town (see 628 Figure 1b for the location), (b) field view of white massive dolomite overlain by the rust 629 color sandstone of the Barzaman Formation near Oil & Gas Research Center outcrops, 630 SQU, scale: the light pole is 4 m high, (c) partially altered peridotite boulder into the 631 dolomite matrix, College of Commerce parking outcrops (CoC parking), SQU, scale: 632 pencil 13 cm long, (d) massive dolomite close view, no sedimentary structures or fossils 633 present, scale: hammer in the red circle is 32 cm long, (e) cluster of red and gray chert 634 clasts in dolomite matrix, scale: the pencil is 13 cm long, (f) unaltered ophiolite clast in 635 the dolomite matrix, scale: car key is 5 cm long, (g) ghost ophiolite clast chemically 636 altered to dolomite, clast boundary marked by the iron leaching, scale: pencil size 13 cm 637 long.



640 Figure 3. (a-b) XRD patterns and SEM images obtained from selected samples, calcite

<sup>641 (</sup>OC9) and (c-d) dolomite (CC2).



Figure 4. Post Archean Australian Shale (PAAS) normalized REE+Y concentrations of all
the carbonate samples (color-coded solid lines; Barzaman Formation, Oman; this study),
mean values of bulk oceanic crust and lower crust (circles; White & Klein, 2014), Oman
ophiolite (Girardeau et al., 2002), seawater (triangles, South Pacific Station 12, 2m depth;
Zhang & Nozaki, 1996) and groundwater (squares; pH = 8.5, Al Khod area, Oman; Semhi
et al., 2009). PAAS values are taken from McLennan (2001).







Figure 5. (a) Plot of Pr/Pr\* vs. Ce/Ce\* showing six different sections to differentiate
between La and Ce anomalies interpreted as: I) no anomaly; IIa) positive La-anomaly
produces apparent negative Ce-anomaly; IIb) negative La-anomaly produces apparent
positive Ce-anomaly; IIIa) real positive Ce-anomaly; IIIb) real negative Ce-anomaly; IV)
positive La-anomaly conceals positive Ce-anomaly. (b) A plot of Ce\* (Ce-anomaly) vs.
Ce/Ce\* and Pr/Pr\* ratios.



659 Figure 6. Plot of Cr/Ni vs. Ni/V showing data of carbonate samples (this study),

groundwater from Al Khod area (Semhi et al., 2009) and ultramafic materials from

various locations (e.g., global MORB, bulk oceanic crust, lower crust, oceanic basins

662 including Atlantic, Pacific and Indian; White & Klein, 2014).



664 Figure 7. Carbon and oxygen isotope plot showing red open circles (this study) along 665 with data of various lithofacies from the Oman-UAE region (small symbols are plotted 666 for reference, representing different lithofacies, for example, ancient travertines, soil 667 zone, travertine, modern travetines, efflorescence, limestone, carbonate crust; Kelemen et al., 2011, Stephen, 2014). The dashed rectangular area represents the isotopic equilibrium 668 zone (Falk et al., 2016). The red-dotted line shows the  $\delta^{13}$ C<sub>VPDB</sub> composition of 669 670 atmospheric CO<sub>2</sub>. The red-filled circle represents the composition of atmospheric CO<sub>2</sub> 671 taken from Friedman and O'Neil (1977). The blue-dotted line represents the expected 672  $\delta^{13}$ C composition of calcite precipitating in equilibrium with the limestone-derived water 673 (pH = 7-8; Stephen, 2014) shown as blue-filled circle (see text for details). The calculated 674 composition of calcite formed as a result of kinetic fractionation (Stephen, 2014) is 675 shown as a green-filled circle. Large open symbols in the equilibrium rectangle represent



677 circle = magnesite veins, Stephen, 2014; square = calcite veins, Stephen, 2014; diamond

- 678 = breccia, Stephen, 2014; triangle = travertines and magnesite and calcite veins, Kelemen
- et al., 2011). Open-blue circles are the isotopic values of CaCO<sub>3</sub> estimated at different
- temperatures (0 to 45°C) using the  $\delta^{18}$ O of water (Stephen, 2014) and the  $\delta^{13}$ C of
- atmospheric CO<sub>2</sub> using the equilibrium fractionation factors given by Deines et al.,
- 682 (1974). Note that there is a substantial variation in  $\delta^{13}$ C compositions (descending),

however,  $\delta^{18}$ O values remain constant (i.e., ~27‰) as the temperature increases.

684



685

**Figure 8.** Temperatures estimated for carbonate samples from various locations using

 $\delta^{18}$ OvPDB and  $\delta^{18}$ OvSMOW of carbonate samples (this study) and compositions of different

- water types (Stephen, 2014) such as alkaline (AW), seawater (SW), ophiolite-derived
- 689 (ODW), hyperalkaline (HAW), limestone aquifer (LAW), and limestone-derived
- 690 (LDW). Estimated temperatures for all the samples from all locations increase
- 691 consistently with the change of water composition in the order LDW < LAW <
- 692 ODW/HAW < AW/SW. Numbers in the brackets represent the number of samples from

- 693 each location. Abbreviations: dol = dolomite. cal = calcite. foss lime = fossiferrous
- 694 limestone.
- 695

# 696 **Table 1.** Details of samples collected from different locations on Sultan Qaboos

- 697 University (SQU) campus and along the nearby Wadi Al Khod representing the
- 698 Barzaman Formation, Oman.

Sample Name	Locality	Coordinates	Lithological Unit	Major phases
BL1	SQU, Behind library	23°35′32″N 58°10′51″E	Conglomerate containing large ophiolite boulders in	dolomite
BL2	SQU, Behind library	23°35′32″N 58°10′51″E	Conglomerate containing large ophiolite boulders in clay matrix	calcite, dolomite
B1.S1	SQU, College of Commerce	23°35′21″N 58°09′35″E	White colour limestone containing corals, algea and other marine fauna	fossiliferous limestone
B1.S2	SQU, College of Commerce	23°35′21″N 58°09′35″E	White color limestone containing corals, algea and other marine fauna	fossiliferous limestone
CC2	SQU, College of Arts and Social Sciences parking	23°35′28″N 58°09′38″E	White to buff colour clay with scattered chert clasts	dolomite
CC3	SQU, College of Arts and Social Sciences parking	23°35′28″N 58°09′38″E	White to buff colour clay with scattered chert clasts	dolomite
OC9	SQU, Oil and Gas Institute	23°35′43″N 58°10′40″E	White hard, compact clay with abundant chert, and ophiolite clasts	calcite
OC10	SQU, Oil and Gas Institute	23°35′43″N 58°10′40″E	White hard, compact clay with abundant chert, and	calcite
Kd1	Wadi Al Khod	23°35′57″N 58°08′35″E	White colour massive carbonate containing abundant chert and altered ophiolite clast	dolomite
Kd2	Wadi Al Khod	23°35′57″N 58°08′35″E	White color massive carbonate containing abundant chert and altered ophiolite clast	dolomite
Kd3	Wadi Al Khod	23°35′57″N 58°08′35″E	White color massive carbonate containing abundant chert and altered ophiolite clast	dolomite
Kd5	Wadi Al Khod	23°35′57″N 58°08′35″E	White color massive carbonate containing abundant chert and altered ophiolite clast	dolomite
Kd7	Wadi Al Khod	23°35′57″N 58°08′35″E	White color massive carbonate containing abundant chert and altered ophiolite clast	dolomite, calcite

Kd8	Wadi Al Khod	23°35′57″N 58°08′35″E	3°35′57″N White color massive 8°08′35″E carbonate containing abundant chert and altered ophiolite clast			
Kd10	Wadi Al Khod	23°35′57″N 58°08′35″E	White color massive carbonate containing abundant chert and altered ophiolite clast	dolomite, calcite		

# **Table 2.** Geochemical data of carbonate rocks from the Barzaman Formation, Oman.

							major	oxides (	wt.%)						
	BL1	BL2	B1.S1	B1.S2	CC2	CC3	OC9	OC10	Kd1	Kd2	Kd3	Kd5	Kd7	Kd8	Kd10
CaO	17.7	33.2	45.6	46.3	27.1	21.3	44.7	37.6	27.9	25.4	25.1	24.9	30.8	28.6	30.7
MgO	13.0	6.70	0.63	1.1	16.8	13.6	1.58	7.15	17.6	17.8	18.2	17.3	14.4	18.6	15.8
$Al_2O_3$	4.76	3.14	0.40	0.71	0.67	0.65	0.92	0.86	1.18	1.05	0.79	1.39	0.70	0.31	0.60
$Fe_2O_3$	2.62	1.32	0.30	0.32	0.44	0.38	0.47	0.39	0.99	0.68	0.45	0.89	0.38	0.21	0.41
$K_2O$	0.12	0.06	0.04	0.04	0.06	0.06	0.04	0.05	0.03	0.04	0.38	bdl	0.04	001	0.01
MnO	0.13	0.07	0.07	0.08	0.15	0.16	0.03	0.03	0.06	0.04	0.04	0.07	0.02	0.01	0.06
$P_2O_5$	0.007	0.009	0.007	0.008	0.006	0.007	0.009	0.009	bdl	bdl	0.007	bdl	0.01	bdl	0.007
Na <sub>2</sub> O	0.93	0.46	0.18	0.25	2.61	3.49	0.16	0.04	0.07	0.05	0.95	0.03	0.05	0.08	0.02
						tra	ace elem	ents (ppr	n)						
As	0.78	0.90	0.36	0.25	0.20	0.17	0.32	0.26	3.36	0.55	0.14	0.94	0.45	bdl	0.30
Ba	38.9	51.5	9.13	26.4	23.5	39.0	25.7	17.4	26.7	69.4	11.4	103	22.4	19.1	89.5
Be	0.28	0.15	0.06	0.07	0.15	0.18	0.14	0.17	0.27	0.16	0.15	0.19	0.13	0.12	0.11
Bi	0.04	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.02	0.01	bdl	0.01
Cd	0.28	0.24	0.45	1.17	0.32	0.32	0.11	0.06	0.23	0.19	0.04	0.09	0.06	0.08	0.07
Co	28.4	25.5	4.25	5.95	16.4	15.1	9.20	7.00	17.5	14.4	13.5	14.5	7.68	4.30	15.9
Cr	495	235	101	66.2	41.5	28.5	59.8	53.9	95.7	248	194	288	83.1	76.8	135
Cs	0.23	0.19	0.06	0.11	0.13	0.10	0.19	0.17	0.10	0.11	0.05	0.10	0.12	0.03	0.05
Cu	22.7	14.5	3.75	6.88	11.3	7.14	6.50	5.80	15.7	12.2	8.70	11.9	8.15	8.10	10.2
Ga	5.36	3.08	0.64	0.96	0.92	0.99	1.21	1.07	1.71	1.36	0.94	1.61	1.00	0.42	0.73
Hf	0.55	0.19	0.05	0.06	0.12	0.10	0.21	0.17	0.14	0.14	0.09	0.15	0.11	0.07	0.07
Nb	1.82	0.66	0.42	0.35	0.39	0.35	0.89	0.80	0.53	0.49	0.35	0.53	0.40	0.18	0.25
Ni	315	172	60.4	68.1	102	87.3	69.2	74.5	220	236	176	199	121	128	145
Pb	1.46	0.72	0.71	1.15	1.44	0.81	1.91	0.95	1.94	1.27	1.20	0.89	0.92	0.51	1.34
Rb	3.50	1.94	1.08	1.32	1.80	1.32	2.10	1.84	1.13	1.13	1.29	1.03	1.68	0.35	0.55
Sb	3.98	3.39	1.92	4.89	2.14	1.58	2.26	3.58	5.14	5.45	3.16	1.25	8.20	0.08	8.01
Sc	12.9	7.70	1.35	1.73	1.95	1.75	2.10	2.00	3.15	3.20	2.45	3.80	1.90	1.20	2.00
Sr	190	147	133	119	326	160	133	252	261	355	343	250	296	264	229
Та	0.13	0.06	0.05	0.04	0.04	0.03	0.07	0.07	0.06	0.09	0.05	0.06	0.05	1.87	0.03
Th	0.60	0.29	0.11	0.16	0.37	0.20	0.50	0.45	0.30	0.24	0.20	0.30	0.24	0.13	0.20
U	0.27	0.13	0.18	0.26	0.40	0.38	0.18	0.35	0.17	0.30	0.19	0.18	0.24	0.21	0.15
V	43.3	18.0	12.9	9.50	10.6	23.3	13.9	12.6	25.6	25.5	15.2	17.4	8.13	4.43	10.5
Zn	51.7	39.9	33.1	139	32.8	31.2	6.05	3.88	26.5	26.4	7.42	7.37	6.38	4.83	5.65
Zr	18.8	6.70	2.00	2.26	4.20	3.72	7.89	6.25	4.78	5.20	3.67	5.72	4.22	2.68	2.47
	rare earth elements + yttrium (ppm)														

La	2.61	1.70	0.93	1.39	1.45	1.59	2.38	1.74	3.35	1.45	1.29	1.57	1.12	1.18	0.95
Ce	5.73	2.69	1.32	1.67	2.64	2.76	4.95	3.48	5.12	2.72	2.19	2.29	2.04	0.87	1.47
Pr	0.79	0.52	0.21	0.37	0.37	0.37	0.59	0.43	0.88	0.39	0.33	0.41	0.28	0.26	0.24
Nd	3.59	2.39	0.94	1.63	1.62	1.64	2.44	1.71	3.90	1.71	1.43	1.81	1.13	1.13	1.05
Sm	0.99	0.65	0.22	0.43	0.40	0.39	0.55	0.37	0.96	0.41	0.35	0.46	0.26	0.25	0.25
Eu	0.33	0.25	0.07	0.13	0.14	0.13	0.14	0.09	0.31	0.14	0.11	0.16	0.08	0.07	0.09
Gd	1.12	0.82	0.26	0.47	0.51	0.53	0.57	0.39	1.07	0.50	0.42	0.56	0.29	0.32	0.29
Tb	0.20	0.14	0.04	0.08	0.08	0.09	0.09	0.06	0.17	0.08	0.07	0.09	0.05	0.04	0.05
Dy	1.30	0.92	0.27	0.46	0.53	0.53	0.53	0.34	1.03	0.52	0.41	0.60	0.32	0.27	0.29
Y	7.03	5.77	1.84	2.93	3.53	4.01	3.09	2.01	5.57	3.29	2.59	3.95	2.27	2.22	1.96
Но	0.26	0.19	0.06	0.09	0.11	0.11	0.11	0.07	0.21	0.11	0.09	0.13	0.07	0.06	0.06
Er	0.76	0.56	0.16	0.26	0.30	0.31	0.30	0.20	0.57	0.31	0.24	0.37	0.21	0.16	0.17
Tm	0.11	0.08	0.02	0.03	0.04	0.04	0.04	0.03	0.08	0.04	0.03	0.05	0.03	0.02	0.02
Yb	0.72	0.50	0.13	0.21	0.25	0.24	0.25	0.17	0.48	0.27	0.21	0.31	0.19	0.12	0.15
Lu	0.10	0.08	0.02	0.03	0.04	0.04	0.04	0.03	0.07	0.04	0.03	0.05	0.03	0.02	0.02
						r	ratios + a	nomalie	s						
Ce*	-0.07	-0.21	-0.20	-0.30	-0.11	-0.12	-0.04	-0.05	-0.19	-0.11	-0.14	-0.21	-0.09	-0.48	-0.18
Ce/Ce*	0.91	0.65	0.69	0.53	0.83	0.83	0.96	0.93	0.68	0.83	0.77	0.66	0.84	0.36	0.71
Pr/Pr*	0.96	1.07	1.02	1.16	0.99	0.97	0.96	0.99	1.06	0.99	1.02	1.07	1.03	1.25	1.04
Y/Ho	19	21	-	15	16	20	14	16	18	13	12	-	10	9	-
Cr/Ni	1.57	1.36	1.68	0.97	0.41	0.33	0.86	0.72	0.43	1.05	1.10	1.45	0.69	0.60	0.93
Ni/V	0.64	0.73	0.60	1.03	2.46	3.07	1.16	1.38	2.30	0.95	0.91	0.69	1.46	1.67	1.07

 $\overline{\left|_{l_e}\right\rangle}$  after German and Elderfield (1990), Morad and Felitsyn (2001).

$$Ce^{*}_{*} = log \left[ \frac{3 \times \left( \frac{Ce_{sample}}{Ce_{shale}} \right)}{2 \times \left\{ \left( \frac{La_{sample}}{La_{shale}} \right) + \left( \frac{Nd_{sample}}{Nd_{shale}} \right) \right\}} \right]$$

$$Ce_{/Ce^*} = \frac{\binom{Ce_{sample}}{Ce_{shale}}}{\left\{0.5 \times \binom{La_{sample}}{La_{shale}} + 0.5 \times \binom{Pr_{sample}}{Pr_{shale}}\right\}} \text{ and } Pr_{/Pr^*} = \frac{\binom{Pr_{sample}}{Pr_{shale}}}{\left\{0.5 \times \binom{Ce_{sample}}{La_{shale}} + 0.5 \times \binom{Nd_{Nd_{shale}}}{Pr_{shale}}\right\}} \text{ after Bau}$$

703 and Dulski (1996).

704 bdl = below detection limit.

705

702

#### 706 Table 3. Carbon and oxygen isotopic data of carbonate rocks from the Barzaman

707 Formation, Oman.

Sample ID	$\delta^{13}C_{VPDB}$ (‰)	$\delta^{18}O_{VPDB}$ (‰)	$\delta^{18}O_{VSMOW}$ (‰)
BL1	-8.00	-6.65	24.1
BL2	-8.28	-8.29	22.4
Bl.S1	-8.60	-7.58	23.1
B1.S2	-8.53	-7.46	23.2
CC2	-7.77	-3.48	27.3
CC3	-7.99	-3.90	26.9
OC9	-9.93	-7.63	21.5
OC10	-9.00	-7.63	22.8
Kd1	-7.87	-5.39	25.4
Kd2	-8.37	-6.08	24.6
Kd3	-8.67	-6.79	23.9
Kd5	-8.29	-6.36	24.4
Kd7	-8.16	-6.21	24.5
Kd8	-8.76	-6.35	24.4
Kd10	-8.66	-6.53	24.2