# Carbonation of mantle peridotites at the Atlantis Massif: Insights from IODP Expedition 357

Lotta Ternieten<sup>1</sup>, Gretchen Früh-Green<sup>1</sup>, and Stefano M. Bernasconi<sup>2</sup>

<sup>1</sup>ETH Zurich <sup>2</sup>ETH-Zurich

November 21, 2022

#### Abstract

Petrographic and major element investigations on carbonates from drill cores recovered during IODP Expedition 357 on the Atlantis Massif (AM) provide information on the genesis of carbonate minerals in the oceanic lithosphere. Textural sequences and mineralogical assemblages reveal three distinct types of carbonate occurrences in ultramafic rocks that are controlled by (i) fluid composition and flow, (ii) temperature of the system, and (iii) the presence of mafic intrusions. The first occurrence of carbonate consists of different generations of calcite that formed syn- to post- serpentinization. These calcites formed at temperatures between 30 and 185°C (based on clumped isotopes) and from a fluid influenced by interaction with mafic intrusions. The second occurrence consists of magnesite, dolomite, calcite and aragonite veins that also formed syn- to post serpentinization. These carbonates formed at temperatures between 4 and 188°C and from fluids with highly variable composition and Mg/Ca ratios, but overall high CO2 and moderate SiO2 concentrations. High FeO (3.3 wt%) and MnO (7.3 wt%) contents indicate high temperatures, high water/rock ratios, and low oxygen fugacity for both carbonate assemblages. The third occurrence consists solely of aragonite veins formed at low-temperatures (5°C) within the uplifted serpentinized peridotites. Chemical data suggest that aragonite precipitated from cold seawater, which underwent little exchange with the basement. Combining these observations, we propose a model that places different carbonate occurrences in a conceptual frame involving mafic intrusions in the peridotites and fluid heterogeneities during progressive exhumation and alteration of the AM.

1	
2	
3	Carbonation of mantle peridotites at the Atlantis Massif: Insights from IODP
4	Expedition 357
5	
6	Lotta Ternieten <sup>1</sup> , Gretchen L Früh-Green <sup>1</sup> and Stefano M Bernasconi <sup>1</sup>
7	
8	<sup>1</sup> Department of Earth Science, ETH Zurich, Clausiusstrasse 25, 8092, Zurich, Switzerland.
9	
10	Corresponding author: Lotta Ternieten (lotta.ternieten@erdw.ethz.ch)
11	
12	Key Points:
13	• A conceptual model places carbonate formation in a time frame with mafic intrusions and
14	fluid heterogeneities during hydration of the AM
15	• CO <sub>2</sub> capture is limited in the shallower crust, concentrated around the active LCHF, but
16	may be more extended in deeper circulation
17	• Magnesite and dolomite formed at high Mg/Ca ratios and zones of channelled flow in
18	serpentinized peridotites at the Atlantis Massif

## 19 Abstract

Petrographic and major element investigations on carbonates from drill cores recovered during 20 IODP Expedition 357 on the Atlantis Massif (AM) provide information on the genesis of carbonate 21 minerals in the oceanic lithosphere. Textural sequences and mineralogical assemblages reveal 22 three distinct types of carbonate occurrences in ultramafic rocks that are controlled by (i) fluid 23 composition and flow, (ii) temperature of the system, and (iii) the presence of mafic intrusions. 24 The first occurrence of carbonate consists of different generations of calcite that formed syn- to 25 post- serpentinization. These calcites formed at temperatures between 30 and 185°C (based on 26 clumped isotopes) and from a fluid influenced by interaction with mafic intrusions. The second 27 occurrence consists of magnesite, dolomite, calcite and aragonite veins that also formed syn- to 28 post serpentinization. These carbonates formed at temperatures between 4 and 188°C and from 29 fluids with highly variable composition and Mg/Ca ratios, but overall high CO<sub>2</sub> and moderate SiO<sub>2</sub> 30 31 concentrations. High FeO (3.3 wt%) and MnO (7.3 wt%) contents indicate high temperatures, high water/rock ratios, and low oxygen fugacity for both carbonate assemblages. The third occurrence 32 33 consists solely of aragonite veins formed at low-temperatures (5°C) within the uplifted serpentinized peridotites. Chemical data suggest that aragonite precipitated from cold seawater, 34 which underwent little exchange with the basement. Combining these observations, we propose a 35 model that places different carbonate occurrences in a conceptual frame involving mafic intrusions 36 37 in the peridotites and fluid heterogeneities during progressive exhumation and alteration of the AM. 38

## 39 **1 Introduction**

Mantle peridotites undergo hydrothermal alteration when exposed to aqueous fluids at mid-40 ocean ridges (MORs), continental margins, subduction zone fore-arcs, and ophiolites, which has 41 significant consequences for the thermal structure and rheology of the oceanic lithosphere, 42 geochemical budgets of the ocean, and microbial processes within and at the seafloor (e.g., Früh-43 Green et al., 2004; Kelley & Früh-Green, 2001; Lister, 1972; Proskurowski et al., 2006; Wheat & 44 Mottl, 2004). Seawater circulation through the ocean crust occurs at rates such that circulation of 45 the entire volume of the ocean through the oceanic crust requires less than 20 Myr (German & Von 46 47 Damm, 2003; Wheat & Mottl, 2004). The resulting hydrothermal alteration of peridotites leads to the formation of hydrous silicates, oxides, sulfides and carbonates (e.g., Frost, 1985). 48

The mechanisms that drive carbonate precipitation have been a subject of study for many 49 50 years (Frost, 1985; Greenwood, J., 1967; Hansen et al., 2005; Hess, 1933; Koons, 1981; Korzhinskii, 1959; Schandl & Naldrett, 1992; Trommsdorff & Evans, 1977). Carbonates can 51 precipitate over a wide range of pressure and temperature conditions and in various settings. In 52 shallow parts of the oceanic lithosphere, carbonates can form during conductive heating of 53 seawater, conductive cooling of hydrothermal fluids, mixing of hydrothermal fluids with seawater, 54 and metasomatic replacement reactions (e.g., Alt et al., 2013; Bach et al., 2011; Grozeva et al., 55 2017; Klein et al., 2015; Schroeder et al., 2015; Schwarzenbach, Früh-Green, et al., 2013). More 56 recently, carbonate formation has received considerable attention as a means to sequester 57 atmospheric CO<sub>2</sub> and reduce global warming (Kelemen et al., 2011; Seifritz, 1990). Previous 58 59 studies indicate that 5 - 9% of the rocks exposed along slow- and ultraslow-spreading MORs consist of hydrothermally altered peridotite (Cannat et al., 2010; Carlson, 2001) that can host 60 carbonates. This makes carbonate formation in ultramafic rocks a potentially significant sink for 61 carbon in the shallow oceanic lithosphere, but one that remains poorly quantified. 62

63 Several field, experimental and theoretical studies have been conducted with the main 64 focus on the carbonation of olivine to magnesite (Andreani et al., 2009; Bruni et al., 2002; Cipolli 65 et al., 2004; Giammar et al., 2005; Hansen et al., 2005; Hövelmann et al., 2011; Kelemen & Matter, 66 2008; King et al., 2010; Klein & Garrido, 2011; Klein & McCollom, 2013; Lafay et al., 2014; Van 67 Noort et al., 2013; Paukert et al., 2012; Peuble, Andreani, et al., 2015). Magnesite formation is a 68 widespread alteration reaction of hydrothermally altered peridotites on land and can be found

mainly within ophiolites in orogenic belts and exhumed mélange rocks in paleo-subduction zones 69 (Barnes et al., 1973; Beinlich et al., 2012; Bohlke, 1989; Boschi et al., 2009; Dabitzias, 1980; Falk 70 & Kelemen, 2015; Hansen et al., 2005; Naldrett, 1966; Robinson et al., 2005; Schandl & Wicks, 71 1991; Spandler et al., 2008; Ulrich et al., 2014), or within highly serpentinized peridotites that 72 have been affected by low-temperature alteration by Mg- and HCO<sub>3</sub>-rich meteoric waters (Barnes 73 & O'Neil, 1969; Bruni et al., 2002; Kelemen et al., 2011; Kelemen & Matter, 2008; Paukert et al., 74 2012; Schwarzenbach et al., 2016). However, magnesite precipitation in oceanic peridotites has 75 only been described in a few studies (Gablina et al., 2006). Instead, aragonite, calcite and less 76 commonly dolomite are reported from hydrated mafic and ultramafic rocks in oceanic settings 77 (Bach et al., 2011; Bonatti et al., 1974; Eickmann, Bach, Rosner, et al., 2009; Kelemen et al., 2011; 78 Ludwig et al., 2006; Schroeder et al., 2015; Schwarzenbach, Lang, et al., 2013). Hydration and 79 80 alteration experiments with ultramafic rocks show that dolomite or magnesite do not precipitate even in supersaturated systems in which dolomite and magnesite formation is thermodynamically 81 82 predicted (Grozeva et al., 2017; Hövelmann et al., 2011). Grozeva et al. (2017) assumed that the Mg/Ca ratio of the reacting fluid at the mineral scale ultimately controls whether magnesite, 83 84 dolomite, or calcite forms in seafloor serpentinization systems. In contrast, Hövelmann et al. (2011) suggest that kinetic factors impede the formation of Mg-bearing carbonates relative to Ca-85 86 carbonates. It is known that during hydrothermal alteration of mantle peridotites, differences in fluid flow significantly change the local solution chemistry, which in turn affect carbonate 87 88 formation. However, it remains unclear what factors directly control carbonate mineralogy in a natural system and what role fluid-rock interactions play during carbonate precipitation. 89

Here we present a study of serpentinized peridotites and metabasic rocks from the Atlantis 90 Massif (AM) close to the Lost City Hydrothermal Field (LCHF) that were recovered during 91 International Ocean Discovery Program (IODP) Expedition 357 (Früh-Green et al., 2017). The 92 Lost City Hydrothermal Field located on the southern wall of the Atlantis Massif is considered an 93 end-member for serpentinite-hosted, hydrothermally active systems at the slow-spreading Mid-94 Atlantic Ridge (MAR). It is an off-axis, low-temperature, peridotite-dominated submarine venting 95 environment driven by seawater migration along deeply penetrating fault systems that facilitate 96 hydration of the plutonic crust and serpentinization of the upper mantle (Kelley et al., 2001, 2005). 97 Similar to other hydrothermal systems, the LCHF is characterized by fluids that are strongly 98 enriched in Ca and depleted in Mg (e.g., Seyfried et al., 2015), whereby Ca is believed to be derived 99

from dissolution of pyroxene (Douville et al., 2002; Gamo et al., 2001; Kelley et al., 2005) or related to silica metasomatism of surrounding mafic domains (Berndt et al., 1989; Bischoff & Dickson, 1975). However, unlike fluids venting from unsedimented, basalt-hosted hydrothermal systems that are typically enriched in CO<sub>2</sub> (Von Damm et al., 1998; Lilley et al., 2003), the LCHF fluids are highly alkaline and depleted in CO<sub>2</sub>, suggesting that they have lost oxidized carbon at depth, either due to metasomatic replacement of minerals or precipitation of carbonates (Proskurowski et al., 2008).

107 In this study, we investigated the carbonate population at the Atlantis Massif to constrain 108 the composition and physico-chemical properties of the precipitating fluid (e.g., Bonatti et al., 1980; Eickmann, Bach, Rosner, et al., 2009; Früh-Green et al., 2003) and to better understand the 109 hydrothermal evolution of the Atlantis Massif. We performed detailed analyses of the chemical 110 and petrological characteristics of the carbonates within the basement, which highlight the 111 112 complexity of this unique system and allow us to examine the crucial roles that protolith and fluid composition play in regulating carbonate formation during interaction of hydrothermal fluids and 113 114 peridotite.

## 115 2 Geological setting and sampling

The Atlantis Massif, located at 30°N along the slow-spreading Mid-Atlantic Ridge (MAR), 116 is a 1.5-2 Myr old, dome-like massif forming the inside corner of the intersection between the 117 MAR and the Atlantis Transform Fault (ATF) (Figure 1). The massif is interpreted as an oceanic 118 core complex (OCC), comprised of lower crustal and upper mantle rocks that were uplifted and 119 exposed by long-lived, low-angle detachment faulting (Blackman et al., 1998, 2002; Cann et al., 120 1997; Karson et al., 2006). Three lithologic domains can be distinguished: the corrugated central 121 122 dome comprising mafic rocks ranging from olivine-rich troctolites to oxide gabbros; the variably altered peridotite-dominated southern wall with intermittent mafic plutonic intrusions, which is 123 124 part of the Southern Ridge and defines the edge of the ATF; and the eastern basaltic block, which 125 is interpreted as the hanging wall of the OCC. The summit peak rises to depths of less than 750 m and is located about midway along the length of the Southern Ridge. The top of the massif is 126 covered by pelagic sediments, rubble, and sedimentary breccias (Blackman et al., 2002; Boschi et 127 al., 2006; Früh-Green et al., 2003; Karson et al., 2006; Schroeder et al., 2002). 128

The Lost City Hydrothermal Field is located on a fault-bounded terrace just below the top 129 of the southern wall near the summit. It is composed of numerous active and inactive, up to 60 m 130 tall, carbonate-brucite chimneys that vent low-temperature (40 - 95°C), alkaline (pH 9 - 11) fluids 131 (Kelley et al., 2001, 2005; Ludwig et al., 2006; Seyfried et al., 2015). The vent fluids are 132 characterized by low silica, metal and CO<sub>2</sub> concentrations and high CH<sub>4</sub> (1 - 2 mmol/kg), H<sub>2</sub> (up 133 to 15 mmol/kg), Ca (~30 mmol/kg), and low-molecular-weight hydrocarbons concentrations. 134 Hydrothermal circulation is believed to be driven by residual crustal heat and lithosphere cooling, 135 with the composition of the fluids controlled by subsurface serpentinization reactions in the 136 underlying mantle rocks. The hydrothermal activity has been on-going for at least 30,000 years 137 (Früh-Green et al., 2003; Kelley et al., 2001, 2005) and subsequent U - Th analyses indicated that 138 this is a minimum age as some of the carbonate deposits yielded ages of up to 120,000 years 139 140 (Ludwig et al., 2011).



141

142 Figure 1. Map of the Atlantis Massif, located at the inside corner of the intersection between the 143 Mid-Atlantic Ridge and the Atlantis Transform Fault, showing the locations of the study sites

144 (M0068, M0069, M0070, M0071, M0072, M0073, M0074, M0075, M0076) drilled during IODP

145 Expedition 357 (Früh-Green at al., 2017). The black square indicates IODP Site U1309 (IODP

Expeditions 304 and 305, Blackman et al., 2006). The black star indicates the location of the Lost
City Hydrothermal Field (Kelley et al., 2001).

148

149 2.1 IODP Expedition 357

IODP Expedition 357 drilled seventeen shallow boreholes (from 1.3 mbsf to maximum 150 151 16.4 mbsf) at nine sites along an east-west trending transect across the Atlantis Massif (Figure 1). Two sites are on the eastern end of the southern wall (Sites M0068 and M0075), three along the 152 centre of the southern wall north of the LCHF (Sites M0069, M0072, and M0076), two on the 153 western end (Sites M0071 and M0073), and two north of the southern wall (Sites M0070 and 154 155 M0074) in the direction of the central dome of the massif and Integrated Ocean Drilling Program Site U1309. Overall, the recovered ultramafic rocks reveal a high and heterogeneous degree of 156 157 serpentinization, as well as metasomatic talc-amphibole-chlorite overprinting and local rodingitization (Früh-Green et al., 2017, 2018). Contacts between ultramafic rocks and gabbroic 158 domains are marked by silica metasomatism with the appearance of talc, tremolite and chlorite 159 (central IODP Holes M0068B, M0072B and M0076B) in part replacing pyroxenes, which 160 indicates that hydration at some sites may have started at temperatures in the range of 400 - 500°C 161 162 and that pyroxene alteration pre-dates the onset of serpentinization (Rouméjon, Früh-Green, et al., 2018; Schroeder & John, 2004). Field and geophysical studies estimated that at least  $\sim 20$  % of the 163 massif is completely serpentinized (Detrick & Collins, 1998; Früh-Green et al., 2003; Nooner et 164 al., 2003), whereby two main stages dominate serpentinization. All harzburgites and dunites have 165 undergone an initial stage of pervasive serpentinization, at 200 - 350°C (Boschi et al., 2008; 166 Rouméjon, Früh-Green, et al., 2018; Rouméjon, Williams, et al., 2018). The second stage of 167 serpentinization is dominated by localized fluid pathways and more focused and intense fluid-rock 168 interaction leading to recrystallization and vein formation dominated by chrysotile or antigorite 169 (Rouméjon, Früh-Green, et al., 2018). 170

This study focuses mainly on the five sites containing altered peridotite (Sites M0071, M0072, M0069, M0076 and M0068, Figure 2). The four remaining sites include foraminiferabearing carbonate ooze, rubble blocks of variable lithologies and sedimentary breccia with volcanic clasts and carbonate sediments (Früh-Green et al., 2017). The sites considered here have a core recovery ranging between 30 % (Hole M0071C) and 75 % (Hole M0069A), with an average

- recovery of 58 %. Drill cores of IODP Expedition 357 are described in detail in Früh-Green et al.
- 177 (2017, 2018, supplementary material), and Rouméjon, Früh-Green, et al. (2018, supplementary
- 178 material).



Figure 2. Simplified downhole logs of the dominant lithologies recovered in the seven holes 180 containing serpentinized peridotites. The western and eastern sites exhibit rubbly intervals and 181 sedimentary structures pointing to a mass-wasting origin and local faulting. The central sites 182 represent in-situ portions of the detachment footwall (Früh-Green et al., 2017; Rouméjon et al., 183 2018a). Serpentinized peridotites from Hole M0071A, M0069A and M0068B are dominated by 184 aragonite veins. In contrast, serpentinites from Hole M0072B have dominantly calcite and Mg-185 rich calcite occurring in veins and serpentinized olivine cores, and one dolomite vein. Hole 186 M0076B is the only hole that exhibits aragonite, calcite, Mg-rich calcite, dolomite and magnesite 187

veins, as well as dolomite in serpentinized olivine cores. The 37 white dots indicate locations ofthin section samples.

190

## 191 **3 Analytical methods**

Petrographic investigations were made on 37 double-sided, polished thin sections of 192 representative samples distributed over five sites (7 holes), covering the diversity of rock types 193 and alteration textures. The sample-set consists of 24 peridotites (21 harzburgites and 3 dunites), 194 nine mafic rocks (4 gabbroic rocks, 5 doleritic rocks), two talc-amphibole  $\pm$  chlorite schists and 195 two brecciated samples. Sample locations within the drill holes are indicated in Figure 2, together 196 with a simplified lithostratigraphy and location of identified carbonate occurrences. Samples are 197 named according to the IODP style guide: Expedition Driling-Platform, Site, Hole\_Core, 198 Coretype Section Interval in cm; (e.g., 357 M0076B 9R 1 5-9, Table 1). For simplicity, we 199 have removed the expedition and drilling platform information that remains the same for all 200 201 investigated samples (e.g., 76B 9R 1 5-9). We use clumped isotope data and radiocarbon ages from a parallel study that investigates the identical set of carbonate veins (Ternieten et al., in prep.). 202

## 203 3.1 Powder X-ray diffraction

For mineralogical identification of carbonate veins, rock samples were cleaned with 2-204 propanol and compressed air. In the first step, the surfaces of the veins were removed and 205 discarded, followed by sampling of the veins. The carbonate powder was homogenized by hand 206 using an agate mortar previously cleaned with dichloromethane (DCM). Crystallographic analyses 207 were made using a Bruker AXS D8 Advance Powder X-ray Diffractometer (XRD) equipped with 208 209 a Lynxeye superspeed detector (Bruker Corporation, Billerica, United States) with Cu Ka X-ray radiation 20 ranging between 10° to 60°, a voltage of 45 kV and a current of 40 mA, step size of 210 0.01°, and measurement time of 1 s per step. Quantification of the mineralogy of powdered 211 212 samples was carried out using the program PowDll (Kourkoumelis, 2013) and the RRUFF database (Lafuente et al., 2015). 213

214 3.2 Optical and electron microscopy

Petrographic analyses were conducted using a polarizing microscope (Carl Zeiss Microscopy GmbH, Göttingen, Germany) on polished thin-sections. Characterization, distribution and textures of carbonates on polished thin-sections were conducted using a cold cathode cathodoluminescence (CL) CL8200 Mk5-2 (Cambridge Image Technology Ltd, Hertfordshire, UK) with a Nikon microscope (Nikon, Japan) interfaced with a Zeiss Axiocam camera (Carl Zeiss Microscopy GmbH, Göttingen, Germany). Operation conditions were set at an accelerating voltage of 15 kV with a beam current of 250 to 300 µA.

Major element composition of selected carbonates was determined using a five-222 223 spectrometer JEOL JXA-8200 and JEOL JXA-8230 Electron Probe Microanalyser (EPMA) (JEOL, Akishima, Japan) operating in wavelength-dispersion mode with an accelerating voltage 224 225 of 15 kV and a current of 10 nA to 5 nA. EPMA analyses were carried out on polished and carboncoated thin sections. Beam diameter was 10 µm, 5 µm and 2 µm, and count times varied from 20 226 to 60 s per element. The program Probe for EPMA (Probe Software Inc., Eugene, United States) 227 was used along with the time-dependent intensity (TDI) correction to counteract the effect of beam 228 229 damage when a drift in the intensity was observed. The mean atomic number background 230 correction was used to correct for the background (Donovan et al., 2016; Donovan & Tingle, 1996). Elements analyzed are Si, Mg, Al, Ba, Ca, Fe, Mn and Sr calculated based on a set of natural 231 and synthetic standards. For most elements with concentrations > 1 wt%, average precision is 232 better than 1 %, and the average accuracy is better than 2 %. The data are quoted as oxide-weight 233 234 per cent. Analyses of phases that yielded SiO<sub>2</sub> concentrations above 0.1 wt% have been excluded from our study, as they likely reflect mixed phases with surrounding serpentine or other silicate 235 minerals. Because crystal size was commonly very small, it is difficult to obtain good analyses by 236 electron microprobe, and twenty-three analyses of dolomite, replacing the cores of olivine crystals, 237 with  $SiO_2 < 4$  wt%, are included here. 238

Carbonate mineralogy	arg, cc lla, cc llb, dol - - - -	cc* - cc*	c c c c c c c c c c c c c c c c c c c	cc III, dol cc cc IIa, cc IIb cc IIb, dol, mgs arg, cc III, cc IIb, dol, mgs	arg* - - ates replacing the cores of
f the Atlantis Massif. Carbonate occurrences	Carb vein	inter. carb - inter. carb carb vein	inter. carb inter. carb inter. carb inter. carb inter. carb carb vein, repl. core carb vein, repl. core carb vein, repl. core carb vein, repl. core carb vein, repl. core	carb vein, repl. core carb vein, inter. carb carb vein carb vein carb vein carb vein	carb vein - - in veins, repl. core = carbon
1 mafic rocks from the southern wall o Type of the rock	Serpentinized dunite Serpentinized harzburgite Serpentinized harzburgite Serpentinized harzburgite Serpentinized harzburgite Serpentinized harzburgite Dolerite	Metadolerite Metadolerite Metadolerite Serpentinized harzburgite	Rodingitized gabbro Rodingitized dolerite Talc/amphi/chlorite schist Talc/amphi/chlorite schist Rodingitized gabbro Serpentinised harzburgite Serpentinized harzburgite Serpentinized harzburgite Serpentinized harzburgite Serpentinized harzburgite	Serpentinized dunite Serpentinized dunite Metagabbro Serpentinized harzburgite Serpentinized harzburgite Serpentinized harzburgite Serpentinized harzburgite Serpentinized harzburgite Serpentinized harzburgite Metagabbro	Serpentinized harzburgite Serpentinized dunite Serpentinized dunite apy agnesite; carb vein = carbonates precipitated
n ultramafic and Depth (mbsf) top bot.	0.45 0.48 3.71 3.73 3.71 3.73 0.46 0.50 3.35 3.45 3.70 3.74 5.12 5.15 7.58 7.61 10.33 10.37	8.25 8.39 9.87 9.90 11.46 11.50 16.08 16.10	7.86 7.89 8.37 8.39 9.02 9.04 9.54 9.57 10.38 10.42 10.90 10.93 11.40 11.43 11.77 11.81 11.77 11.81 11.200 12.02 12.02 12.02 12.28 12.33	4.22 4.27 7.28 7.32 7.50 7.53 8.61 8.63 9.16 9.20 10.32 10.34 12.05 12.32 12.66 12.22 12.96 12.63 12.66 12.92 12.96 15.50 15.70	0.10 0.13 4.84 4.87 7.60 7.62 inescence microsco dolomite, mgs = n
mineralogy i Interval (cm) top bot.	45 46 57 67 77 67 70 23 70 74 70 74	137 151 127 130 14 18 14 16	15 66 55 55 55 56 72 50 51 50 51 50 51 50 51 50 51 50 51 50 51 50 51 50 51 50 51 50 51 50 51 50 51 50 51 50 50 50 50 55 55 55 55 55 55 55 55 55	78 83 55 59 77 80 63 65 118 122 960 962 960 962 112 148 151 148 151 91 111	10 13 84 87 3 5 and cathodolum
nate occurrences and Site Core Hole Section	71 A 1 71 B 3 71 C 2 71 C 2 77 C 2 77 C 2 77 C 2 77 C 2 77 C 3 77 C 3 77 C 4 71 C 4 71 C 4 71 C 4 71 C 4 71 C 7 71 C 4 71 C 7 71	69 A 5 1 69 A 6 1 69 A 8 1 69 A 10 2	72 8 8 7 1 1 2 2 8 8 7 1 1 2 2 8 8 7 2 2 8 8 7 1 1 2 2 8 8 8 7 1 1 1 1 1 2 2 8 8 8 1 1 2 2 2 8 8 8 1 1 2 2 2 8 8 8 2 2 2 2	76 8 3 1 76 8 5 1 76 8 5 1 76 8 6 1 76 8 6 1 76 8 6 1 76 8 8 1 76 8 8 1 76 8 8 1 76 8 8 1 76 8 9 1 76 8 9 1 76 8 10 1	68 B 1 1 68 B 4 1 68 B 7 1 eralogy based on optical s = calcite, mg-cc = Mg-rid
Table 1. Carbo Sample	71A-1R1-02 71B-3R1-02 71C-1R1-01 71C-2R1-01 71C-2R1-01 71C-3R1-02 71C-5R1-01 71C-6R1-03.3	69A-5R1-01.3 69A-6R1-01 69A-8R1-01 69A-10R2-01	72B-6R1-01 72B-6R1-02 72B-7R1-01 72B-7R1-01 72B-7R1-03 72B-8R1-01 72B-8R1-01 72B-8R1-02 72B-8R2-01 72B-8R2-01 72B-8R2-01 72B-8R2-013	768-3R1-01 768-5R1-05 768-6R1-01 768-6R1-01 768-6R1-01 768-5R1-01 768-8R1-01 768-8R1-02 768-9R1-03 768-10R1-03.3	68B-1R1-01 68B-4R1-01 68B-7R1-01.1 * Carbonate min arg = aragonite, cc

#### 240 **4 Results**

## 241 4.1 Host Rocks

The carbonate veins are hosted in ultramafic, mafic, and clastic sedimentary rocks. Cores 242 from the northwestern (M0071) and most eastern sites (M0068) contain varying proportions of 243 244 ultramafic-, mafic and sedimentary domains that have been interpreted as originating from masswasting and local faulting processes (Früh-Green et al., 2017; Rouméjon, Früh-Green, et al., 2018). 245 Ultramafic and mafic host rocks were recovered from the central part of the southern wall (IODP 246 Sites M0069, M0072, M0076) and are described as *in-situ* portions of the AM indicated by 247 coherent, decimeter- to meter-long sections of cores, as well as consistent structural measurements 248 (Früh-Green et al., 2017, 2018) (Figure 2 and 3a-c). The central sites also make up the deepest 249 boreholes, and the following discussion mainly focuses on observations from these cores. 250

Modal proportions of primary minerals in the peridotites range from 60 % - 100 % olivine, 251 0% - 40% pyroxene (including minor clinopyroxene), and < 1% - 2% spinel (Rouméjon, Früh-252 Green, et al., 2018), however some serpentinized peridotites from Site M0072 have as much as 5 253 to 8 vol% magnetite and differ considerably from other typical ultramafic domains (Figure 3a). 254 Metamorphosed gabbroic and doleritic intrusions are largely altered to tremolite, chlorite, and/or 255 talc, which locally overprint the serpentinization textures. The ultramafic samples are 256 characterized by complex networks of distinct generations of carbonate veins filled with aragonite, 257 calcite, dolomite and/or magnesite. 258

4.2 Carbonate occurrences

Carbonates in the basement of the southern wall occur as (i) interstitial carbonates, (ii) 260 carbonates replacing fully serpentinized olivine cores, and (iii) carbonate veins (Table 1 and Figure 261 2). Carbonate veins were observed in both mafic and ultramafic rocks. Interstitial carbonates were 262 only observed in mafic rocks, and carbonates in olivine cores were only found within serpentinized 263 peridotites. Interstitial carbonates are typically found in metadolerites, talc-amphibole  $\pm$  chlorite 264 schists and metagabbro. Calcite is the only carbonate phase and has grain sizes  $< 20 \mu m$ , except 265 for one metagabbro with carbonate grains < 0.1 mm (Figure 3b and d). Interstitial carbonates are 266 limited to the central sites at the southern wall (M0069, M0072, M0076). Carbonates replacing the 267 core of olivine are dominantly calcite and rarely dolomite and have an average grain size  $< 50 \,\mu m$ 268

- 269 (Figure 3e f). Calcite within the crystal cores is restricted to Site M0072 and can occur as one or
- two generations in the same sample, whereas dolomite is limited to samples from Site M0076.



272	Figure 3. Characteristic petrologic features of host lithologies and carbonates. (a) Thin section
273	scan of fully serpentinized harzburgite with increased magnetite content, calcite I and II veins,
274	and calcite II in olivine cores. Two calcite I veins are cut by later serpentinite vein
275	(72B_8R_2_67-69.5). (b) Thin section scan of metagabbroic host rock with calcite I vein and
276	interstitial calcite I (76B_5R_1_77-80, close-up in Fig. 3d. (c) Thin section scan of fully
277	serpentinized dunite clast hosting fragments of dolomite and calcite II veins, and aragonite with
278	acicular growth within the fossiliferous carbonate sand (71A_1R_1_45-48). (d) Interstitial calcite
279	in metagabbroic sample from Fig.3b (BSE image). (e) Calcite II replaced fully serpentinized
280	olivine (PPL, 72B_8R_CC_0-5, close-up in Fig. 3f). (f) Calcite IIa and IIb in olivine core (BSE
281	image). (g) A network of fibrous aragonite veins crosscut all other textures in the ultramafic host
282	rock (PPL, 69A_10R_2_14-16). (h) Overview of a multigeneration dolomite vein in the
283	ultramafic rock crosscut by later calcite III (PPL, 76B_9R_1_5-9, close-up in Fig. 3i). (i) CL-
284	image of the dolomite vein of Fig. 3h containing multiple generations of dolomite, marked by
285	Roman numerals, and other carbonate phases. Abbreviations: Arg, aragonite; cc, calcite; chl,
286	chlorite; dol, dolomite; hbl, hornblende; mgs, magnesite; mgt, magnetite; serp, serpentine; qtz,
287	quartz.

288

289

#### 4.2.1 Carbonate veins

Veins are the most abundant carbonate occurrence in the Atlantis Massif basement and 290 tend to be concentrated in the central drill sites closest to the LCHF (M0069, M0072, M0076) 291 (Figure 2). The carbonate veins typically dissect grain boundaries, have kinked to irregular shapes, 292 293 and show crosscutting or more rarely branching geometries. They are less than 1 cm wide and are mainly hosted by variably serpentinized peridotites and crosscut most other textures, indicating a 294 late formation stage (Figure 3g, 4a). The abundance of carbonate veins is highly variable and can 295 be as low as one vein or make up to half of a hand sample (~ 40 vol%) as in some ultramafic rocks 296 from Site M0076. The veins are composed of aragonite, calcite, dolomite and magnesite in variable 297 proportions. 298



Figure 4. Sample pictures and photomicrographs of carbonates. (a) Late microcrystalline aragonite 300 vein in serpentinized harzburgite (76B 9R 1 70-73). (b) Calcite II vein in serpentinized dunite 301 (PPL, 72B 8R 2 26-30, close-up in Fig. 4c). (c) Calcite IIa + IIb vein with straight crystal 302 contacts from Fig. 4b (BSE image). (d) A network of magnesite, dolomite and calcite II veins cut 303 by radial growth calcite III (PPL, 76B 8R 1 112-117). (e) CL- image of the carbonate network 304 of Fig. 4d. (f) Dolomite veins in serpentinized harzburgite crosscut by serpentine veins (PPL, 305 76B 5R 1 55-59, close-up in Fig. 4g). (g) Dolomite vein crosscut by serpentinite from Fig. 4f 306 (PPL + CL). (h) CL- image of highly deformed calcite I vein with several lines of secondary fluid 307 inclusions of Fig. 4i (72B 8R 2 26-30, close-up in Fig. 4j). (i) Calcite I vein in serpentinized 308 dunite of Fig 4h (PPL). (j) Multiple secondary fluid inclusions in calcite I vein with small vapour 309 phases of Fig. 5h (PPL). Abbreviations: Cc, calcite; dol, dolomite; mgs, magnesite; mgt, magnetite; 310 311 serp, serpentine.

312

In half of the samples, at least two generations of carbonates coexist in the same vein, whereby two samples 76B\_8R\_1\_112-117 and 76B\_9R\_1\_5-9 show at least four different generations (Figure 3h - i, 4b - c, and 5). The altered mafic rocks are devoid of carbonate veins, except for sample 76B\_5R\_1\_77-80 that contains a narrow (< 50  $\mu$ m) vein of calcite on the outside of the sampled rock piece (Figure 3b). Serpentinites show the highest textural variability of carbonate veins at the AM.

Magnesite, dolomite, and calcite veins are a few mm wide (Figure 3a, h - i, and 4b - i) and 319 320 occur mainly at the central Sites M0072 and M0076, except for one calcite/dolomite vein, found in a sedimentary breccia on top of Hole M0071A (71A 1R 1 45-48, Fig. 3c). Magnesite veins 321 are the least frequent, occurring exclusively in association with dolomite and limited to the deeper 322 sections of Hole M0076B ( > 12 mbsf). Crosscutting relationships indicate that most magnesites 323 pre-date all other carbonates (Figure 4d - e). Dolomite veins are more common at Site M0076; 324 they are < 5 mm wide and precipitated at the rim of multiphase veins or are cut by serpentine + 325 magnetite veins, suggesting an early stage of formation (Figure 3h - i, 4f - g). They differ from the 326 other veins in that they are sometimes formed by multiple generations of dolomite with partly 327 dissolved surfaces and pitted textures (Figure 3i and 5). 328



**Figure 5.** Simplified time log of carbonate vein formation of (a) 76B\_9R\_1\_5-9, (b) 76B\_8R\_1\_112-117 and (c) 72B\_8R\_2\_67-70, based on cold cathodoluminescence microscopy. The Roman numerals (I to III) indicate different generations, letters (a to c) indicate a change in chemical composition or texture. Different generations occur intergrown, with erosive surface contacts or straight crystal contacts; clumped isotope temperatures of carbonate formation and radiocarbon age data from Ternieten et al. (in prep.).

336

Calcite veins are most common at Site M0072, showing the highest textural variability, 337 338 and often occur as two distinct generations within the same vein. At Site M0072, they constitute the earliest carbonate generation with intergrown or straight crystal contacts to the surrounding 339 minerals (Figure 4b - c). Locally calcite veins are intergrown with serpentine; these are highly 340 deformed and exhibit secondary fluid inclusions, suggesting an earlier formation stage (Figure 3a, 341 342 4h - j). The fluid inclusions are composed of an aqueous liquid and a small vapour phase suggesting formation temperatures below 100°C. These veins are limited to the deeper section ( > 11 mbsf) 343 at Hole M0072B. In two samples from Site M0076 (76B 5R 1 55-59, 76B 8R 1 112-117), 344 calcite shows botryoidal textures (Figure 4d - e), which is indicative of growth in open fractures. 345

The most abundant and volumetrically dominant carbonate type are up to 1 cm wide 346 aragonite veins that are observed throughout the ultramafic rocks at Hole M0069A, in the deeper 347 section of Hole M0076B (> 13 mbsf), in the top cores from Holes M0071A and M0068B, and on 348 the altered surface of a deeper sample from Hole M0068B (Figure 2). The aragonite veins crosscut 349 the primary rock fabric (Figure 3g and 4a), also postdate all secondary fabrics and are the last to 350 be formed. Vein aragonite displays three distinct crystal habits: fibrous crystals, acicular crystals, 351 and microcrystalline aragonite (Figure 3c and g, and 4a). The long axes of acicular crystals 352 growing into open spaces and the fibrous crystals are preferentially oriented vertical to the walls 353 of the veins. 354

355 4.3 Carbonate chemistry

A significant observation in the basement rocks is the high variability in composition and distribution of carbonate phases and the presence of distinct generations of carbonates within one sample and/or vein at Holes M0072B and M0076B. The carbonates have distinctly different Fe, Mn, Sr and Mg concentrations which allow distinguishing different generations and indicate local variations in fluid chemistry. Representative chemical analyses of all carbonate phases are presented in Table 2.

Carbonates in the altered mafic rocks exhibit a limited range of major element 362 compositions. Interstitial calcites have negligible MgO, and FeO and MnO concentrations that 363 vary from 0 to 0.3 wt% and from 0 to 0.1 wt%, respectively. The single identified calcite vein 364 within the mafic rock samples only differs slightly by higher MgO concentration of 2.4 to 3.2 wt%, 365 but also shows FeO and MnO concentration < 0.1 wt% (Table 2). In contrast, the carbonates within 366 the serpentinized ultramafic rocks show greater textural and chemical variations. Magnesite veins 367 have FeO concentrations ranging from 0.6 to 1.3 wt% and MnO concentrations from 2.4 to 4.1 368 wt% (Fig. 6a - b). These FeO and MnO patterns are within the range of dolomite and calcite 369 370 compositions. The dolomite veins have slightly more variable FeO and MnO concentrations 371 compared to magnesite and lower FeO compared to calcites (FeO = 0 to 0.9 wt%, MnO = 0 to 6.0wt%, Fig. 6a - b). Sample 76B 9R 1 5-9, which contains a multiphase dolomite vein (Figure 3h 372 - i), has distinctly higher MnO contents at the rim compared to the centre ( $MnO_{rim} = 6.0 \text{ wt\%}$ , 373  $MnO_{centre} = 3.0$  wt%; Fig. 6b). 374

Table 2. R	epresentativ	e analyses c	of carbonate i	n ultramafic	and mafic r	ocks from t	he southern	wall at the <i>i</i>	Atlantis Mas	ssif.		
Sample	76B_5R_1, 77-80	76B_5R_1, 77-80	69A_10R_2, 14-16	72B_8R_1, 69-72	72B_8R_1, 69-72	72B_8R_2, 67-70	72B_8R_2, 67-70	72B_8R_2, 26-30	$76B_9R_1$ , $5-9$	$76B_9R_1$ , $5-9$	76B_5R_5, 55-59	$76B_9R_1, 5-9$
Hole	M0076B	M0076B	M0069A	M0072B	M0072B	M0072B	M0072B	M0072B	M0076B	M0076B	M0076B	M0076B
Host rock	Mafic	Mafic	Ultramafic	Ultramafic	Ultramafic	Ultramafic	Ultramafic	Ultrmafic	Ultamafic	Ultramafic	Ultramafic	Ultramafic
Phase	Calcite	Calcite	Aragonite	Calcite IIb	Calcite IIb	Calcite IIa	Calcite IIa	Calcite I	Calcite III	Dolomite	Dolomite	Magnesite
Occurrence	Vein	Interstitial	Vein	Vein	Repl. core	Vein	Repl.core	Vein	Vein	Vein	Repl.core	Vein
(wt%)												
SiO	0.01	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.15	0.10
MgÕ	2.78	0.04	0.00	0.20	1.52	14.72	14.84	0.03	4.42	20.41	20.27	44.03
Al,O,	0.01	0.02	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.00
BaO	0.00	0.05	0.00	0.00	0.00	0.00	0.01	0.01	000	0.00	0.00	0.00
$FeO_{tot}$	0.09	0.21	0.00	0.07	0.34	1.23	1.07	0.12	0.02	0.17	0.58	0.64
MnO	0.00	0.05	0.00	0.93	1.42	4.71	4.00	0.01	2.06	3.43	1.96	4.04
SrO	0.06	0.07	0.52	00.0	0.00	0.01	0.01	0.03	0.06	0.00	0.01	0.00
CaO	52.64	55.61	55.23	54.89	52.65	33.16	33.91	55.86	48.93	28.86	26.84	0.11
co,	44.42	43.93	44.25	43.90	44.06	46.17	46.16	43.94	44.51	47.13	47.13	51.09
Total	100	100	100	100	100	100	100	100	100	100	100	100
Abbreviation	<pre>h: repl. core = c</pre>	carbonates rep	lacing cores of e	complete serpe	ntinized olivir	les						

The calcite veins show pronounced variations in Mg, Fe and Mn and, in combination with 376 petrographic observations, can be classified into three groups. Calcite I is almost pure CaCO<sub>3</sub>; it 377 constitutes the earliest carbonate phase and the only phase where we observed fluid inclusions (see 378 section 4.2.1). They have low SrO, MgO, FeO and MnO concentrations of < 0.2 wt%, which is 379 similar to the interstitial calcites observed within the mafic rocks and distinguish them from other 380 calcites within the ultramafic lithologies (Figure 7a and c). The most common calcites, especially 381 at Site M0072, are classified as calcite II. Two subgroups can be distinguished based on the Mg 382 concentration: Calcite IIa with MgO > 11.9 wt%, and calcite IIb with MgO < 7.3 wt%. FeO and 383 MnO contents vary from 0 to 3.3 wt% and from 0 to 7.3 wt%, respectively (Figure 7a - d). Calcite 384 IIa also shows higher Fe and Mn concentrations than calcite IIb in some samples at Site M0072, 385 whereas such distinct variations between the subgroups were not observed at Site M0076. The 386 subgroups show no unique chronology, and depending on the location, either calcite IIa or calcite 387 IIb represents the earlier phase. Calcite III veins are defined by concentrations of MgO of 2.2 to 388 6.3 wt%, FeO of < 0.2 wt%, and a wide range of MnO contents from 0 to 3.6 wt%. They are limited 389 to Site M0076 and are the more common calcite type at this site where they represent the last or 390 391 one of the latest carbonate phases, often occurring within open fractures as botryoidal crystals (Figure 4d - e, 5 and 7b and d). Aragonites throughout all cores have uniform compositions with 392 393 MgO and MnO below the detection limit, only minor FeO concentrations < 0.1 wt% and variable to high SrO concentrations (0.4 - 2.5 wt%, Table 2). In comparison, all other carbonate phases 394 395 have SrO concentrations of less than 0.2 wt%.

The major element patterns of carbonates replacing fully serpentinized olivine cores are 396 indistinguishable from the vein carbonates. Calcite IIa and IIb that replace olivine and/or 397 serpentine show Fe and MnO contents from 0.2 to 2.0 wt% and 0.8 to 7.3 wt%, respectively, with 398 calcite IIa showing the highest MnO concentrations (> 2.7 wt%). This is similar to calcite IIa in 399 the veins; however, a distinct separation between the calcite subgroups based on their FeO content 400 cannot be made (Figure 7e - f). No calcite I or calcite III were identified replacing olivine cores 401 and or serpentine. The dolomites replacing olivine have a uniform and much lower manganese 402 concentrations than the replacive calcites (MnO = 1.7 to 2.3 wt%). FeO contents vary from 0.4 to 403 1.1 wt%, which is within the same range as dolomite occurring in veins (Table 2). 404



**Figure 6.** Variations in (a) FeO versus MgO content and (b) MnO versus MgO content of carbonate veins hosted by serpentinized peridotites from two samples of Hole M0076B from the southern wall at the Atlantis Massif (76B\_8R\_1\_112-117, 76B\_9R\_1\_5-9). The ultramafic rocks show a diverse assemblage of carbonate phases in one sample (aragonite, calcite, dolomite, magnesite). Pictures of the samples in Fig. 3h and i, and Fig. 4d and e. Clumped isotope temperatures of carbonate formation and radiocarbon age data from Ternieten et al. (in prep).

412

## 413 4.3.1 Carbonate generations

Cathodoluminescence (CL) in carbonates results from trace-element substitution for Ca<sup>2+</sup> 414 and Mg<sup>2+</sup> and is the most suitable method to identify different carbonate generations with only 415 minor chemical variations. Although various trace elements are capable of influencing carbonate 416 CL (Machel, 1985), the ion Mn<sup>2+</sup> is the most critical "activator", and Fe<sup>2+</sup>, Fe<sup>3+</sup>, Ni<sup>2+</sup>, and Co<sup>2+</sup> are 417 common "quenchers" (Götze, 2012). The intensity and colour of luminescence are dependent on 418 the relative proportions of Mn and Fe (Barnaby & Rimstidt, 1989). Additionally, the stimulated 419 luminescence bands depend on the position in the crystal structure in which the  $Mn^{2+}$  ion is 420 integrated (Mg<sup>2+</sup> or Ca<sup>2+</sup> position) (Götze, 2012). Thus, the same MnO content can result in 421 different CL. This is particularly well illustrated in Figure 5, which shows simplified time logs of 422 carbonate vein formation of three different samples based on CL investigations. Six carbonate 423 generations with dolomite, magnesite, calcite III, and aragonite (Figure 5a) were identified in 424

Sample 76B 9R 1 5-9 (Figure 3h - i). Dolomite is characterized by multiple generations within 425 a single vein, and we identified three generations with partial dissolution and pitted textures 426 between them and separated by magnesite precipitation. Dolomite veins from this sample showed 427 significant variations in the MnO content ( $MnO_{dol} = 1.9$  to 6.0 wt%) and only a limited range of 428 FeO from of 0.1 to 0.3 wt%, which makes variations in  $Mn^{2+}$  concentration the most likely cause 429 for the differences in luminescence (Figure 6a - b). Sample 76B 8R 1 112-117 (Figure 4d - e) 430 contains four different generations with magnesite, dolomite, calcite IIa and calcite III (Figure 5b). 431 Similar to sample 76B 9R 1 5-9, dolomite is the volumetrically dominant carbonate phase in this 432 sample; however, the vein network is much finer, and no distinct generations within the dolomite 433 can be identified. This coincides with homogeneous MnO and FeO content of the dolomite (Figure 434 6a - b). However, both samples show a decrease in the FeO content with time from 0.6 to 1.0 wt% 435 in the earliest generations of magnesite to < 0.1 wt% in the latest aragonites and calcite III. Sample 436 72B 8R 2 67-70 (Figure 3a) is representative for Hole M0072B and contains three generations 437 of calcite: calcite I, calcite IIa, calcite IIb (Figure 5c). The different generations observed by CL 438 are also reflected by distinct major element compositions (Figure 7a and c). In addition, calcite IIa 439 and IIb show a decreasing FeO content with time from  $FeO_{cc IIa} = 1.2$  wt% to  $FeO_{cc IIb} = 0.3$  wt%, 440 similar to samples from Hole M0076B. 441

442

Figure 7. Variations in FeO and MnO versus MgO content of calcite veins hosted by serpentinized peridotites from the southern wall at the Atlantis Massif of (a and c) Hole M0072B and (b and d) Hole M0076B, and of carbonates replacing fully serpentinized serpentine olivine cores from Hole M0072B (e and f). Clumped isotope temperatures of carbonate formation from Ternieten et al. (in prep). The dashed lines mark the difference between calcite IIa and IIb. Black symbols in figure (e and f) represent the chemical composition of calcite veins from the same sample.



## 451 **5 Discussion**

Carbonation reactions in serpentinized peridotites are controlled by temperature, protolith 452 composition and activities of dissolved constituents, and are particularly influenced by fluctuations 453 in  $aSiO_{2(aq)}$  and  $aCO_{2(aq)}$ . Figure 8 shows two activity-activity diagrams depicting phase relations 454 in the MgO-CaO-SiO<sub>2</sub>-H<sub>2</sub>O-CO<sub>2</sub> system. It has long been recognized that serpentinized peridotites 455 are highly reactive in the presence of dissolved CO<sub>2</sub> (Johannes, 1967, 1969), and with increasing 456  $aCO_{2(aq)}$ , the characteristic alteration assemblage of serpentine + brucite will successively be 457 replaced by serpentine + magnesite, followed by talc+magnesite and finally quartz + magnesite 458 459 (Figure 8a) (e.g., Boschi et al., 2009; Hansen et al., 2005). Even at low temperatures, moderate concentrations of CO<sub>2(aq)</sub> are sufficient to dissolve brucite in favour of carbonate. Thermodynamic 460 models and experimental studies show that the  $aSiO_{2(aq)}$  and  $aCO_{2(aq)}$  are intimately linked and 461 will ultimately affect silicate mineral stabilities, Mg/Ca ratios in the fluids and thus the 462 composition of the precipitating carbonate (e.g., Frost & Beard, 2007; Grozeva et al., 2017; 463 Hövelmann et al., 2011). Low  $aMg^{2+}$  will favour the precipitation of calcite, whereas high 464 concentrations of CO<sub>2</sub> and Mg<sup>2+</sup> in the fluids will favour dolomite and magnesite precipitation 465 (Figure 8) (Grozeva et al., 2017). 466

467 Altered peridotites were recovered in all seven holes drilled across the AM southern wall. The exceptional core recovery preserved multiple carbonate generations that allow the 468 reconstruction of the alteration history. One of the most remarkable features is the high variability 469 in composition and distribution of carbonate phases, including magnesite, dolomite, calcite and 470 471 aragonite. The diverse carbonate phases record progressive fluid infiltration and alteration during extension, unroofing and uplift of the AM and the simultaneous evolution from pervasive- to 472 localized serpentinization. Figure 9 shows an interpretative cross-section of the Atlantis Massif, 473 highlighting the most critical processes affecting alteration and carbonate formation of the oceanic 474 core complex. Previous studies (e.g., Boschi et al., 2006; Karson et al., 2006; Rouméjon, Früh-475 Green, et al., 2018) showed that the alteration of the AM is affected by seawater infiltration via 476 grain boundary flow and a complex network of steeply dipping normal faults. Fluids are focused 477 along the detachment fault zone and discrete ductile shear zones triggering serpentinization and 478 silica metasomatism of serpentinites and gabbros, resulting in talc-amphibole-chlorite schist 479 480 lenses. Different carbonate occurrences are characteristic for different locations within the AM 481 and timing during its uplift. Black squares within Figure 9 indicate locations that are recorded by

samples from the different drill holes. A conceptual model for the hydrothermal evolution of the 482 AM is presented in Figure 10, which summarizes the alteration history of the peridotites that are 483 in proximity to mafic intrusions (Figure 10.1 - 10.3) compared to those in the periphery to 484 intrusions (Figure 10.4 - 10.6). Our model follows work of Rouméjon and Cannat (2014), who 485 argued that the combination of anisotropic thermal contraction and tectonic stresses in the brittle 486 domain of the mantle leads to pervasive micro-fracturing of peridotites at mid-ocean ridges. This 487 provides an efficient permeability network of pathways for serpentinization and initial carbonate 488 precipitation. 489



490

Figure 8. Activity-activity diagrams depict phase relations in the MgO-CaO-SiO<sub>2</sub>-H<sub>2</sub>O-CO<sub>2</sub> 491 system at 300°C and 35 MPa modified after Grozeva et al. (2017). Numbered stars indicate 492 potentially compositions of fluids from the three central sites representing distinct alteration 493 conditions at the Atlantis Massif; 1 = strong influence of mafic intrusion (M0072B), 2 = minor494 influence of mafic intrusion (M0076B), 3 = alteration of abyssal peridotites (M0069A). (a) The 495 plot of log  $aSiO_{2(aq)}$  vs log  $aCO_{2(aq)}$  showing the stability fields of various silicate minerals and 496 carbonates. Continuous lines denote equal activities of phases in the MgO-H<sub>2</sub>O-CO<sub>2</sub> system. 497 Dashed blue lines indicate equal activities of phases in the MgO-CaO-H<sub>2</sub>O-CO<sub>2</sub> system. The Fluid 498 composition of M0072B moved to higher  $aSiO_{2(aq)}$  and  $aCO_{2(aq)}$  values over time. (b) The plot of 499  $\log aMg^{2+}$  vs  $\log aCa^{2+}$ . The fluid composition of M0076B moved out of the stability field of 500

magnesite and into the stability field of calcite with successively uplift and alteration of the AM.
 Reprint from Grozeva et al. (2017), Copyright 2017, with permission from Elsevier.

503

504

## 5.1 Alteration heterogeneities along the southern wall of the Atlantis Massif

505 Our detailed petrological, textural and geochemical observations point to three main 506 controlling factors that affect carbonate precipitation at the Atlantis Massif: (i) fluid composition 507 and flux, (ii) temperature of the system, and (iii) presence of mafic intrusions. We focus on the 508 three central sites (M0069, M0072, M0076), each of which provides distinct pieces of information 509 about the complex history of fluid infiltration and alteration during exhumation of the massif.

510 5.1.1 Carbonate formation in the presence of mafic intrusions

Interlayers of mafic intrusions are most prevalent at Hole M0072B, which shows the highest degree of silica metasomatism, marked by talc-, amphibole- and chlorite-rich domains, and which provides the best information about the influence of mafic intrusions on fluid and carbonate chemistry. This hole is characterized by a lack of magnesite and dolomite in the ultramafic rocks, which suggest that  $Mg^{2+}$  transport was strongly limited in the proximity of the metasomatic interlayered mafic intrusions and was locked into other silicate alteration assemblages (Figure 10, frame 1 - 3).

At Hole M0072B, the initial carbonate phase is calcite I, which formed syn-518 serpentinization and is intergrown with serpentine in veins (Figure 10.2). The lack of magnesite 519 and dolomite suggests that removal of Mg<sup>2+</sup> resulted in low Mg/Ca ratios and favoured calcite 520 precipitation (Figure 8b) (e.g., Hövelmann et al., 2011; Lumsden et al., 1995; Peuble, Godard, et 521 al., 2015). Alteration of mafic intrusions and an associated static replacement of serpentine by talc 522 has been previously identified at the Atlantis Massif (Boschi et al., 2006; Rouméjon, Früh-Green, 523 et al., 2018). Talc formation can result from either Si-addition to or Mg-removal from the 524 serpentinized peridotite. Previous studies (Bach et al., 2004; Boschi et al., 2006; Rouméjon, Früh-525 Green, et al., 2018) assumed that Si-addition rather than Mg-removal is responsible for talc 526 527 formation, given that the alteration of mafic rocks releases significant amounts of silica compared with ultramafic rocks (Malvoisin, 2015; Wetzel & Shock, 2000). The metasomatism of gabbro and 528 dolerites in the peridotites provide a source of Ca<sup>2+</sup> and SiO<sub>2</sub> from the dissolution of plagioclase 529

and pyroxenes and removal of Mg<sup>2+</sup> through talc formation (Berndt et al., 1989; Bischoff & 530 Dickson, 1975). In an experimental study at 400°C, Allen and Seyfried (2003) showed that high-531 temperature alteration could lead to a faster dissolution of clinopyroxene compared to olivine, 532 providing an additional input of  $SiO_2$  and  $Ca^{2+}$  and lower input of  $Mg^{2+}$ . Elevated temperatures in 533 the subsurface of the Atlantis Massif are indicated by the oxygen isotope composition of serpentine 534  $(\delta^{18}O_{\text{recrystallized serp}} = 1.6 \text{ to } 2.9 \%$ , Rouméjon, Williams, et al., 2018) which correspond to 535 formation temperatures between 320 and 360°C (assuming  $\delta^{18}$ Ofluid = 2.4 ‰, Rouméjon, Williams, 536 et al., 2018) and which would be sufficient for clinopyroxene dissolution. Calcite I veins yield one 537 of the highest carbonate formation temperatures of all carbonates across the AM ( $T_{A47} = 145$  to 538 185 °C) and indicate that temperatures in the hydrothermal system remained high during later 539 alteration. We propose that the hydrothermal fluid in proximity to silica metasomatism is depleted 540 in  $Mg^{2+}$  and in combination with moderate  $aCO_2$  and the dissolution of clinopyroxene with slower 541 olivine serpentinization was sufficient to maintain low Mg/Ca ratios in the hydrothermal fluid and 542 prevent magnesite and dolomite precipitation. Calcite I veins have MgO, FeO, and MnO 543 concentrations below the detection limit, which distinguish them from other carbonates at the AM 544 and suggests that all dissolved Mg<sup>2+</sup>, Fe<sup>2+</sup>, and Mn<sup>2+</sup> was taken up by secondary silicate minerals 545 (serpentine, talc, chlorite). 546

Calcite II is the second carbonate phase at Hole M0072B and occurs post-serpentinization 547 within veins or replacing serpentine and/or olivine (Figure 10.3). Calcite II has higher MgO 548 contents, which may be linked to an increase in Mg/Ca ratio resulting from an addition of 549 unmodified seawater in the evolved hydrothermal fluids. A higher influx of seawater increase 550  $CO_{2(aq)}$  and  $Mg^{2+}_{(aq)}$  concentrations, shifting the equilibrium towards the Mg-carbonate stability 551 fields (Figure 8a). This may also lead to faster dissolution rates of the primary minerals of the 552 mafic and ultramafic rocks, which can add additional SiO<sub>2</sub>, Mg<sup>2+</sup> and Ca<sup>2+</sup> to the fluids. Calcite II 553 is separated into two subgroups, a Mg-rich calcite IIa and a Mg-poor calcite IIb (Figure 7). Calcite 554 IIb precipitates from a fluid with lower  $Mg^{2+}_{(aq)}$  concentration in areas where silica alteration 555 minerals consumed more Mg<sup>2+</sup><sub>(aq)</sub> from solution. The Mg-rich calcite IIa precipitated from a fluid 556 that was more influenced by serpentinization resulting in higher Mg<sup>2+</sup> concentrations probably in 557 more peripheral areas of the mafic intrusions. Some veins contain both calcite II subgroups, but 558 559 without a clear chronology. This may reflect changes in the influence of the mafic intrusions on

- the composition of the fluids over time, by either changes in the fluid pathway or variations in
- 561 dissolution and/or formation rates of primary and secondary minerals.



563 Figure 9. Interpretative cross-section of the Atlantis Massif, showing fluid pathways, metasomatic zones, and extent and development of serpentinization (light green shaded region and lines) related 564 to detachment faulting and steep normal faults (modified after Karson et al., 2006, Boschi et al., 565 2006, and Rouméjon et al., 2018). The oceanic core complex forms as a result of extension, 566 567 unroofing, and uplifting on the edge of the MAR. The shear zone along the detachment surface is characterized by heterogeneous, variably altered and deformed gabbroic and peridotite lithologies 568 with extensive silica metasomatism. Fluids were focused along the detachment and discrete ductile 569 shear zones triggering metasomatism of serpentinites and gabbros, resulting in talc-amphibole-570 chlorite schist lenses. The footwall shows widespread, ongoing serpentinization related to a 571 complex network of steeply dipping faults that enhance infiltration of seawater into the fresh 572 peridotite promoting the development of pervasive to localize serpentinization and propagation of 573 the serpentinization front, which ultimately lead to the formation of the LCHF. Black squares 574

indicate hypothetical locations within the oceanic core complex of carbonate formation during
 different stages in the hydrothermal evolution of the Atlantis Massif and are detailed in Figure 10.

577

Calcite IIa is not only characterized by higher MgO but also by higher FeO contents (Figure 578 7a). We suggest that high temperatures and higher fluid fluxes may result in elevated  $Fe^{2+}$ 579 concentrations in the fluid and consequently in the calcites. McCollom and Bach (2009) showed 580 581 that high temperatures (T =  $100^{\circ}$ C) and high water/rock ratios (W:R > 2) result in lower concentrations of Fe in the secondary minerals brucite and serpentine, leading to the formation of 582 583 a higher amount of magnetite and H<sub>2</sub> (see also Malvoisin, 2015). This may also result in higher Fe<sup>2+</sup> concentration in solution. In fact, at the Atlantis Massif, higher magnetite concentrations (5 584 to 8 vol%) are observed at sites influenced by mafic intrusions. In addition, higher amounts of 585 magnetite have been associated with more oxidizing conditions caused by higher fluid flow 586 (Andreani et al., 2009; Ulrich et al., 2014) supporting the argument of higher water/rock ratios and 587 influx of seawater. High alteration temperatures and increased mixing of fresh seawater in the 588 hydrothermal fluid is also supported by clumped isotope investigations of the same samples 589  $(\delta^{13}C_{cc I} = -2.7 \%, T_{\Delta 47} = 145 \text{ to } 185^{\circ}C; \delta^{13}C_{cc II} = -0.7 \%, T_{\Delta 47} = 145^{\circ}C)$ . Calcite II in olivine 590 cores occurs either dispersed in the rocks or is associated with calcite II veins. The similarity of 591 592 the element patterns suggests that replacive calcite II formed simultaneously from a similar hydrothermal fluid as calcite II in the veins. 593

594

## 5.1.2 Magnesite and dolomite formation within oceanic peridotites

Hole M0076B consists mainly of peridotites and exhibits the highest diversity of carbonate 595 phases, including magnesite, dolomite, calcite and aragonite. The ultramafic rocks of this hole 596 show no evidence of silica metasomatism and thus provide constraints on carbonate formation in 597 598 the absence of mafic intrusions (Figure 10, frame 4 - 6). The first generation of carbonate is either magnesite or dolomite forming syn- to post- serpentinization in veins and/or replacing serpentine 599 and olivine (Figure 10.5). Dolomite, and especially magnesite precipitation, requires high Mg/Ca 600 ratios in the fluids (e.g., Hövelmann et al., 2011; Lumsden et al., 1995; Peuble, Godard, et al., 601 2015). Thermodynamic studies predict that magnesite should form during the reaction of 602 serpentinite and CO<sub>2</sub>-bearing aqueous fluids (e.g., Grozeva et al., 2017; Klein & Garrido, 2011). 603

However, only a few studies have reported magnesite in oceanic serpentinites (Gablina et al., 2006) 604 whereas it is more common in altered ultramafic rocks on land (soapstone and listvenite). Previous 605 studies suggest that magnesite in oceanic settings may form in Ca-poor ultramafic rocks, such as 606 dunite or completely serpentinized peridotite, or where a sustained influx of CO<sub>2</sub>-rich fluids leads 607 to silica activities in the fluid  $(aSiO_{2(aq)})$  exceeding the stability of serpentine and consequently 608 leading to high Mg/Ca ratios in the fluid (Figure 8a) (Barnes & O'Neil, 1969; Grozeva et al., 2017; 609 Klein & Garrido, 2011). However, magnesite veins at the Atlantis Massif are found in highly 610 serpentinized harzburgites with no evidence for serpentine instability. Indeed thermodynamic 611 studies predict that relatively low  $aSiO_{2(aq)}$ , imposed by serpentine and brucite formation and lower 612 dissolution rates of the primary minerals, leads to stabilization of clinopyroxene and thus to lower 613  $Ca^{2+}_{(aq)}$  in the fluids (Figure 8a) (e.g., Klein et al., 2013). Based on thermodynamic models 614 (Grozeva et al., 2017), we argue that high  $CO_{2(aq)}$  and moderate  $SiO_{2(aq)}$  concentrations in the 615 hydrothermal fluid has led to serpentinization of orthopyroxene and olivine, while preserving 616 clinopyroxene, which should have been sufficient to maintain high Mg/Ca ratios and favour the 617 precipitation of Mg-rich carbonates (Figure 8b). 618

Magnesite is absent in most samples, even though high MgO content in calcites indicates 619 high  $Mg^{2+}$  in solution. This suggests that  $CO_{2(aq)}$  concentration alone does not control magnesite 620 precipitation at the Atlantis Massif. An additional factor, such as confined flow pathways with 621 622 limited fluid fluxes may be necessary for magnesite formation. Pokrovsky & Schott (2002) and Schott et al. (2009) showed that a high fluid flux kinetically favours the formation of Ca-rich rather 623 than Mg-rich carbonates, due to different properties of  $Mg^{2+}$  and  $Ca^{2+}$  ions. The limiting step for 624 carbonate crystallization is the dehydration of cations at the crystal surface. The lower the rate of 625 water molecule exchange in the first hydration sphere of a metal ion, the lower the crystallization 626 rate of a metal carbonate. Studies showed that the rate of water molecule exchange from the fluid 627 into the cation hydration sphere is faster for Ca<sup>2+</sup> than Mg<sup>2+</sup> (e.g., Pokrovsky & Schott, 2002), 628 which explains the different precipitation rates of Ca-rich (fast) and Mg-rich (slow) carbonates. 629 Thus, dolomite will precipitate under conditions of moderate fluid fluxes when the fluid contains 630 Ca even in a Mg-rich system, and magnesite will precipitate in rock-dominated systems in zones 631 of more-reduced fluid flow (Peuble, Andreani, et al., 2015). Dolomite replacing serpentine or 632 olivine occurs either dispersed in the rocks or is associated with dolomite veins. The similarity of 633

the element patterns suggests that replacive dolomite formed at the same time from a similarhydrothermal fluid as dolomite in the veins.

The formation of magnesite and dolomite is followed by precipitation of calcite II at Hole 636 M0076B (Figure 10.6). The continuous hydration of the basement can lead to an increase of the 637 activity of SiO<sub>2</sub>, which would lead to a dissolution of clinopyroxene (Figure 8a) and consequently 638 to a lower Mg/Ca ratios in the fluids favouring calcite formation. In addition, a potential higher 639 influx of seawater caused by the progressive uplift of the massif may also result in an increase in 640 fluid fluxes through brittle deformation, which favours the formation of Ca-rich carbonates (see 641 642 magnesite discussion). Both calcite II (calcite IIa, calcite IIb) subgroups are observed (Figure 7b and d), indicating that high  $Mg^{2+}$  concentrations are maintained as the system evolves. The 643 compositional variability of the hydrothermal fluids can be caused by changes in precipitation 644 and/or dissolution rates, in the influx of fresh seawater and changing temperatures. The high 645 variability is also observed in the variable and high FeO and MnO contents of calcite II; whereby, 646 a systematic difference between the subgroups cannot be observed. 647

The last carbonate phases are calcite III and aragonite precipitating in veins (Figure 10.6): 648 They have low FeO contents, which points to precipitation in equilibrium with cold hydrothermal 649 650 fluids and mixing with unaltered seawater. In some cases, the botryoidal texture of calcite III (Figure 4d - e; Figure 6) indicates precipitation from a percolating solution within an open space. 651 These spaces are often fractures crosscutting all minerals and deformation textures of the 652 ultramafic rock, indicating that they formed after tectonic deformation of the serpentinite (Klein 653 et al., 2015). Precipitation from cold, unaltered seawater mixing with evolved hydrothermal fluid 654 is confirmed by clumped isotope temperatures of calcite III of  $T_{\Delta 47} = 1$  to 8°C ( $\delta^{18}O_{cc III} = -4.0$ 655 % VPDB) and seawater like carbon isotopes  $\delta^{13}C_{cc III} = +1.7$  to +2.2 %, and for aragonite by T<sub>Δ47</sub>, 656  $_{arg}$  = 1 to 4°C ( $\delta^{18}O_{arg}$  = ~ 3.9 ‰ VPDB), and a  $\delta^{13}C_{arg}$  = -1.5 to -0.1 ‰. This range also matches 657 the isotopic composition of the carbonate chimneys from the LCHF that are caused by mixing of 658 the venting fluid with the surrounding seawater, and show  $\delta^{13}$ C values close to marine values 659 within 2 per mil of 0 % for most of the samples and  $\delta^{18}$ O values >2 % VPDB (Kelley et al., 2005), 660 which is consistent with late precipitation of calcite III and aragonite. 661



Figure 10. Conceptual model for the development of alteration heterogeneities in domains of the 663 footwall along the detachment fault plane at the Atlantis Massif illustrating (1 to 3) alteration 664 characteristics of Hole M0072B and (4 to 6) representative alteration textures of Hole M0076B. 665 The combination of anisotropic thermal contraction and tectonic stresses in the brittle domain of 666 the mantle leads to pervasive micro-fracturing (Rouméjon et al., 2014), providing a fine network 667 of pathways for serpentinization and carbonate precipitation. Hypothetical location of the 668 illustrated lithologies can be seen in Figure 9. Hole M0072B is characterized by fully serpentinized 669 peridotites with high magnetite concentration and carbonate precipitation in proximity to 670 significant silica metasomatism of gabbroic and peridotite lithologies. The alteration of gabbroic 671 lithologies provides a higher concentration of Ca in the hydrothermal fluid and leads to calcite I, 672 IIa and IIb formation. Calcite I represents carbonate formation during early hydration, whereas 673 calcite IIa and IIb represent later formation. Carbonate precipitation at Hole M0076B is controlled 674 by a high Mg/Ca ratio and zones of reduced flow due to structural heterogeneities, which leads to 675

the early formation of magnesite and dolomite along microfractures. As exhumation and serpentinization proceeds, alteration of clinopyroxene provides enough Ca for calcite IIa formation and less altered seawater leads later to calcite III precipitation inside fractures. See text for a detailed discussion.

680

681

## 5.1.3 Carbonate formation at the periphery of the hydrothermal system

Peridotites at Hole M0069A are covered by  $\sim$ 7 m of sediments and dolerites but do not show evidence for silica metasomatism. Rouméjon, Früh-Green, et al. (2018) showed that the basement at this site is characterized by pervasive serpentinization without late overprinting and recrystallization. Thus, this site provides information on the alteration at the periphery of an active hydrothermal system with low degrees of fluid-rock interactions.

Carbonate is only present in aragonite veins, which are the volumetrically dominant 687 carbonate phase at the AM. Geochemical and textural features are comparable to aragonite from 688 sites in the vicinity of the hydrothermal system. Aragonite formed at low temperatures ( $T_{\Delta 47, arg} =$ 689 1 to 7°C) from fairly unmodified seawater ( $\delta^{13}C_{arg} = -0.2$  to 1.6 %). At such conditions, aragonite 690 precipitation is favoured over calcite due to high  $Mg^{2+}$  and sulfate concentrations (Burton, 1993; 691 Eickmann, Bach, & Peckmann, 2009). The lack of carbonate veins within the dolerite, and the 692 relative high vein density in the peridotites below it, strengthens previous interpretations that 693 dolerite domains constitute impermeable barriers and fluids are channelled along the walls of the 694 intrusion (Rouméjon & Cannat, 2014). 695

5.2 Manganese concentration in carbonates from the Atlantis Massif

Carbonates are in general a favourable sink for Mn (Deer et al., 1992) and hydrothermal 697 systems are important sources of manganese (e.g., Charlou et al., 2002; Klinkhammer et al., 1977). 698 Laboratory studies have shown that seawater tends to leach manganese from mid-ocean ridge 699 basalts at elevated temperatures (T >  $200^{\circ}$ C) and pressures (P > 500 bar), causing an increase of 700 Mn<sup>2+</sup> in solution (Bischoff & Dickson, 1975; Mottl et al., 1979). Previous studies of calcite 701 cements formed in shallow fresh-water aquifers provide evidence that the uptake of Mn<sup>2+</sup> in 702 carbonates is mainly dependent on Eh which controls Mn solubility (Barnaby & Rimstidt, 1989; 703 Dromgoole & Walter, 1990). Most marine low-temperature carbonates have MnO contents of ~1 704

wt% (e.g., Eickmann, Bach, Rosner, et al., 2009; Picazo et al., 2020). At the Atlantis Massif, 705 carbonates exhibit remarkably high and variable MnO concentrations, and we argue that this is 706 caused by a change in the redox state of the hydrothermal fluid. The high MnO contents would 707 indicate a low redox state, typical of serpentinizing environments, and a shift to lower MnO would 708 indicate a progressive increase in Eh. Most carbonate veins at the AM do not show a systematic 709 change with their sequence of precipitation except for a thicker dolomite vein. In this vein, early 710 dolomites have higher MnO (MnO<sub>max, dol</sub> = 6 wt%) than younger generations (Figure 6b), which 711 may indicate a change to higher oxygen fugacity of the fluid over time. This change in fluid 712 composition is also indicated by dissolved surfaces and pitted textures in early dolomites (Figure 713 3i). 714

At the Mid-Atlantic Ridge, carbonates with extremely high MnO contents (max. 9.5 wt% 715 Mn; Schroeder et al., 2015) have been previously reported. Carbonates from ODP Site 1275 (35 716 717 km north of the 15°20' Fracture Zone and 30 km west of the MAR axis) have high MnO contents and were correlated to an early, high-temperature ( $T_{max} = 174^{\circ}C$ ) stage of formation. These 718 carbonate veins occur within gabbros and troctolites, which most likely were the source of the 719 elevated Mn. At the AM, carbonates are less common in the mafic rocks and contain MnO contents 720 below 0.1 wt%. However, we do observe higher MnO ( $MnO_{max, M0072B} = 7.3$  wt%) in carbonates 721 in proximity to mafic intrusions, compared to carbonates that formed in the periphery to mafic 722 723 intrusions. We propose that the high MnO concentrations are consistent with highly reducing serpentinizing fluids at the AM, leaching high amounts of Mn<sup>2+</sup> from the interlayered gabbroic 724 bodies, and transport to domains where cooling of hydrothermal fluids and or mixing with seawater 725 leads to the formation of carbonates. 726

5.3 Carbonates as a  $CO_2$  sink within the oceanic lithosphere

Recently, carbonate formation in ultramafic rocks has received considerable attention as a means to sequester atmospheric CO<sub>2</sub> (e.g., Kelemen & Matter, 2008), and studies of various ophicalcites showed that carbon is stored over millions of years (Bachu et al., 1994; Kelemen et al., 2011; Schwarzenbach, Früh-Green, et al., 2013; Seifritz, 1990). Studies of modern and ancient serpentinites estimate that up to 10 wt% total inorganic carbon is fixed as carbonates during serpentinization and carbonate precipitation, and that approximately 10% of all carbon that is cycled through the ocean is incorporated into the oceanic lithosphere during alteration of oceanic

crust (Alt et al., 2013; Schwarzenbach, Früh-Green, et al., 2013). To better evaluate the potential 735 of ultramafic rocks as long term storage for CO<sub>2</sub>, quantitative information on the sources and sinks 736 of carbon is necessary. One critical factor contributing to the continuing uncertainty on this topic 737 is the difficulty in obtaining samples directly from subsurface environments near mid-ocean ridges 738 for analysis of carbon compounds, and most estimations are based on information inferred from 739 analysis of hydrothermal fluids discharged at the seafloor. Most of these hydrothermal vents have 740 CO<sub>2</sub> concentrations that are substantially higher than the amount of dissolved inorganic carbon 741 (DIC:  $CO_{2(aq)} + HCO_{3} + CO_{3}^{2}$ ) in seawater. However, <sup>13</sup>C and <sup>14</sup>C isotope analyses of CO<sub>2</sub> in 742 hydrothermal fluids from the Endeavour system (high temperature basaltic dominated 743 hydrothermal system) indicates that most of the seawater DIC is removed from circulating fluids 744 and stored as carbonates within the basement before discharge at hydrothermal vents on the 745 seafloor (Proskurowski et al., 2004). It is assumed that this is true for most hydrothermal systems 746 (McCollom, 2008; and references therein). 747

In contrast to basalt-hosted hydrothermal systems, the vent fluids from the Lost City 748 749 hydrothermal system are highly depleted in DIC (Proskurowski et al., 2008), which leads to the assumption that the AM should contain significant carbonate deposits. Thus, one of the main goals 750 of IODP Expedition 357 was to investigate the distribution of carbonate deposits within the 751 basement of the Atlantis Massif. Our results show that the amount of inorganic carbon in the 752 753 shallow basement holes is relatively low. Carbonates are almost exclusively observed close to the active venting LCHF and rarely at other locations along the southern wall. The distribution of 754 carbonates throughout the cores from the central Sites (M0069, M0072, M0076) is heterogeneous 755 with an overall carbonate vein abundance estimated at  $\sim 2$  vol%. However, because the maximum 756 depth reached was 16.4 mbsf, we do not know how high the concentrations are at depth. We 757 propose that most of the DIC removal occurred during deeper circulation of the fluid and that 758 shallow parts of the AM record carbonate precipitation associated with present-day hydrothermal 759 circulation and driven by localized shallow fluid circulation along fractures. 760

Additionally, the AM is a relatively young exhumed mantle sequence, and our study provides evidence that  $CO_2$  uptake by low-temperature aragonite formation is, in general, low at young serpentinized mantle, but may increase if fracturing and veining continue for tens of millions of years. A low abundance of low-temperature aragonite veins in young serpentinized mantle is also observed at ODP Site 895 at Hess Deep (Blusztajn & Hart, 1996), ODP Site 920 south of the Kane Fracture Zone (Alt & Shanks, 1998) and from ODP Site 175 at the Mid-Atlantic

Ridge (Schroeder et al., 2015). The data presented here provide information on the fate of carbon

in the oceanic lithosphere and will help to better evaluate whether hydration and serpentinization

of oceanic crust is a globally significant sink for CO<sub>2</sub>. Further investigations of deeper drill holes

and older oceanic core complexes would be necessary.

## 771 6 Conclusions

772 We investigated the alteration of peridotites in seven drill holes at five sites across the southern wall of the Atlantis Massif recovered during IODP Expedition 357. We developed a 773 conceptual model for the genesis of carbonates in oceanic lithosphere. Detailed textural, 774 mineralogical and geochemical investigations reveal variable alteration between holes that 775 represent different portions of the footwall exhumed in the vicinity of the detachment fault zone. 776 Three characteristic types of carbonate occurrences, including the minerals magnesite, dolomite, 777 calcite and aragonite, could be identified. All occurrences formed close to the actively venting 778 LCHF under different conditions and were controlled by (i) fluid composition and flow, (ii) 779 temperature, and (iii) influence of mafic intrusions. SiO<sub>2(aq)</sub>, CO<sub>2(aq)</sub> and Mg<sup>2+</sup> concentrations of 780 the hydrothermal fluid have particularly significant impacts on the carbonate compositions. 781

Even though carbonates within this oceanic hydrothermal system indicate ubiquitous high 782 Mg<sup>2+</sup> concentrations, only limited amounts of magnesite and/or dolomite, are formed, suggesting 783 that kinetic factors impede the formation of Mg-bearing carbonates relative to Ca-carbonates. This 784 supports the hypothesis that both a high Mg/Ca ratio and confined flow are necessary to precipitate 785 Mg-carbonates. In addition, our study indicate that lower Mg<sup>2+</sup> concentrations in solution 786 characterize hydrothermal fluids in proximity to mafic intrusions. This lower Mg<sup>2+</sup> in solution in 787 proximity to mafic intrusions in combination with the necessary lower fluid flow may limit 788 magnesite formation in the oceanic lithosphere, since we know that hydrothermal systems at mid-789 790 ocean ridges often contain mafic intrusions and are, in general, characterized by high fluid flow 791 (Bach et al., 2011). Therefore, the formation of magnesite in oceanic settings is likely limited to domains of ultramafic rocks without major mafic intrusions and less rapid upflow of hydrothermal 792 fluids. 793

Our study shows that Ca-Mg carbonates, as a significant part of the process of hydration and alteration of oceanic peridotites, represent an important tool to reconstruct alteration histories

of serpentinized peridotites. Moreover, Ca-Mg carbonates may represent a significant sink of 796 carbon from the seawater and or the mantle that would otherwise reenter/enter the oceans. Thus, 797 carbonate-containing oceanic serpentinite transported into subduction zones may represent an 798 additional carbon reservoir recycled into the deep mantle. Age determinations show that shallow 799 carbonates formed over a narrow time interval from 37,000 to 23,000 yr, corresponding to the 800 early stages of the Lost City hydrothermal system (Früh-Green et al., 2003). The active vents at 801 Lost City still show highly depleted DIC contents, which suggests that carbonate is continuing to 802 be formed at deeper levels of this off-axis hydrothermal system. 803

The results of our study are of interest not only for the investigation of ancient and presentday carbonation systems, but they may also be of interest for the interpretation of artificial carbonation of serpentinite on land, at the seafloor or in laboratory experiments. We show that thermodynamically predicted magnesite precipitation occurs locally within oceanic serpentinized and highlights the high heterogeneity of hydrothermal fluids circulating within the footwall exhumed at the Atlantis Massif, and probably in any detachment system.

## 810 Acknowledgements

We would like to thank Madalina Jaggi, Julien Allaz, Lydia Zehnder and Andreas Jallas for help with sample preparation and analyses as well as the European Consortium for Ocean Research Drilling (ECORD) and the IODP Expedition 357 science party for providing drill core samples for this study. We gratefully acknowledge funding by the Swiss National Science Foundation (SNF) project No. 200021\_163187 to Früh-Green. Results of individual analyses of the samples will be available online on PANGAEA (www.pangaea.de).

# 817 **References**

- Allen, D. E., & Seyfried, W. E. (2003). Compositional controls on vent fluids from ultramafichosted hydrothermal systems at mid-ocean ridges: An experimental study at 400°C, 500
  bars. *Geochimica et Cosmochimica Acta*, 67(8), 1531–1542.
  https://doi.org/10.1016/S0016-7037(02)01173-0
- Alt, J. C., & Shanks, W. C. (1998). Sulfur in serpentinized oceanic peridotites: Serpentinization
   processes and microbial sulfate reduction. *Journal of Geophysical Research: Solid Earth*,
   *103*(B5), 9917–9929. https://doi.org/10.1029/98jb00576
- Alt, J. C., Schwarzenbach, E. M., Früh-Green, G. L., Shanks, W. C., Bernasconi, S. M., Garrido,
  C. J., et al. (2013). The role of serpentinites in cycling of carbon and sulfur: Seafloor
  serpentinization and subduction metamorphism. *Lithos*, *178*, 40–54.
  https://doi.org/10.1016/j.lithos.2012.12.006
- Andreani, M., Luquot, L., Gouze, P., Godard, M., Hoisé, E., & Gibert, B. (2009). Experimental
  Study of Carbon Sequestration Reactions Controlled by the Percolation of CO 2 -Rich
  Brine through Peridotites. *Environmental Science & Technology*, *43*(4), 1226–1231.
  https://doi.org/10.1021/es8018429
- Bach, W., Garrido, C. J., Paulick, H., Harvey, J., & Rosner, M. (2004). Seawater-peridotite
  interactions: First insights from ODP Leg 209, MAR 15°N. *Geochemistry, Geophysics, Geosystems*, 5(9). https://doi.org/10.1029/2004GC000744
- Bach, W., Rosner, M., Jöns, N., Rausch, S., Robinson, L. F., Paulick, H., & Erzinger, J. (2011).
  Carbonate veins trace seawater circulation during exhumation and uplift of mantle rock:
  Results from ODP Leg 209. *Earth and Planetary Science Letters*, *311*(3–4), 242–252.
  https://doi.org/10.1016/j.epsl.2011.09.021
- Bachu, S., Gunter, W. D., & Perkins, E. H. (1994). Aquifer disposal of CO2: Hydrodynamic and
  mineral trapping. *Energy Conversion and Management*, *35*(4), 269–279.
  https://doi.org/10.1016/0196-8904(94)90060-4
- Barnaby, R. J., & Rimstidt, J. D. (1989). Redox conditions of calcite cementation interpreted
  from Mn and Fe contents of authigenic calcites. *Geological Society of America Bulletin*, *101*(6), 795–804. https://doi.org/10.1130/0016-7606(1989)101<0795:RCOCCI>2.3.CO;2
- Barnes, I., & O'Neil, J. R. (1969). The relationship between fluids in some fresh alpine-type
  ultramafics and possible modern serpentinization, western United States. *Bulletin of the Geological Society of America*, 80(10), 1947–1960. https://doi.org/10.1130/00167606(1969)80[1947:TRBFIS]2.0.CO;2
- Barnes, I., O'Neil, J. R., Rapp, J. B., & White, D. E. (1973). Silica-carbonate alteration of
   serpentine: Wall rock alteration in mercury deposits of the California Coast Ranges.
   *Economic Geology*, 68(3), 388–398. https://doi.org/10.2113/gsecongeo.68.3.388
- Beinlich, A., Plümper, O., Hövelmann, J., Austrheim, H., & Jamtveit, B. (2012). Massive
  serpentinite carbonation at Linnajavri, N-Norway. *Terra Nova*, 24(6), 446–455.
  https://doi.org/10.1111/j.1365-3121.2012.01083.x
- Berndt, M. E., Seyfried, W. E., & Janecky, D. R. (1989). Plagioclase and epidote buffering of
   cation ratios in mid-ocean ridge hydrothermal fluids: Experimental results in and near the

858	supercritical region. <i>Geochimica et Cosmochimica Acta</i> , 53(9), 2283–2300.
859	https://doi.org/10.1016/0016-7037(89)90351-7
860	Bischoff, J. L., & Dickson, F. W. (1975). Seawater-basalt interaction at 200°C and 500 bars:
861	Implications for origin of sea-floor heavy-metal deposits and regulation of seawater
862	chemistry. <i>Earth and Planetary Science Letters</i> , 25(3), 385–397.
863	https://doi.org/10.1016/0012-821X(75)90257-5
864	Blackman, D. K., Cann, J. R., Janssen, B., & Smith, D. K. (1998). Origin of extensional core
865	complexes: Evidence from the Mid-Atlantic Ridge at Atlantis Fracture Zone. <i>Journal of</i>
866	<i>Geophysical Research: Solid Earth</i> , 103(B9), 21315–21333.
867	https://doi.org/10.1029/98jb01756
868	Blackman, D. K., Karson, J. A., Kelley, D. S., Cann, J. R., Früh-Green, G. L., Gee, J. S., et al.
869	(2002). Geology of the Atlantis Massif (Mid-Atlantic Ridge, 30° N): Implications for the
870	evolution of an ultramafic oceanic core complex. <i>Marine Geophysical Researches</i> ,
871	23(5/6), 443–469. https://doi.org/10.1023/B:MARI.0000018232.14085.75
872	Blusztajn, J. S., & Hart, S. R. (1996). Sr and O Isotopic Ratios of Aragonite Veins from Site 895.
873	<i>Proceedings of the Ocean Drilling Program, 147 Scientific Results, 147</i> , 311–313.
874	https://doi.org/10.2973/odp.proc.sr.147.035.1996
875 876 877 878	Bohlke, J. K. (1989). Comparison of metasomatic reactions between a common CO2-rich vein fluid and diverse wall rocks: intensive variables, mass transfers, and Au mineralization at Alleghany, California. <i>Economic Geology</i> , <i>84</i> (2), 291–327. https://doi.org/10.2113/gsecongeo.84.2.291
879	Bonatti, E., Emiliani, C., Ferrara, G., Honnorez, J., & Rydell, H. (1974). Ultramafic-carbonate
880	breccias from the equatorial Mid Atlantic Ridge. <i>Marine Geology</i> , 16(2), 83–102.
881	https://doi.org/10.1016/0025-3227(74)90057-7
882	Bonatti, E., Lawrence, J. R., Hamlyn, P. R., & Breger, D. (1980). Aragonite from deep sea
883	ultramafic rocks. <i>Geochimica et Cosmochimica Acta</i> , 44(8), 1207–1214.
884	https://doi.org/10.1016/0016-7037(80)90074-5
885	Boschi, C., Früh-Green, G. L., Delacour, A., Karson, J. A., & Kelley, D. S. (2006). Mass transfer
886	and fluid flow during detachment faulting and development of an oceanic core complex,
887	Atlantis Massif (MAR 30°N). <i>Geochemistry, Geophysics, Geosystems, 7</i> (1).
888	https://doi.org/10.1029/2005GC001074
889 890 891 892	Boschi, C., Dini, A., Früh-Green, G. L., & Kelley, D. S. (2008). Isotopic and element exchange during serpentinization and metasomatism at the Atlantis Massif (MAR 30°N): Insights from B and Sr isotope data. <i>Geochimica et Cosmochimica Acta</i> , 72(7), 1801–1823. https://doi.org/10.1016/j.gca.2008.01.013
893 894 895 896	Boschi, C., Dini, A., Dallai, L., Ruggieri, G., & Gianelli, G. (2009). Enhanced CO2-mineral sequestration by cyclic hydraulic fracturing and Si-rich fluid infiltration into serpentinites at Malentrata (Tuscany, Italy). <i>Chemical Geology</i> , <i>265</i> (1–2), 209–226. https://doi.org/10.1016/j.chemgeo.2009.03.016
897	Bruni, J., Canepa, M., Chiodini, G., Cioni, R., Cipolli, F., Longinelli, A., et al. (2002).
898	Irreversible water-rock mass transfer accompanying the generation of the neutral, Mg–

899 900	HCO3 and high-pH, Ca–OH spring waters of the Genova province, Italy. <i>Applied Geochemistry</i> , 17(4), 455–474. https://doi.org/10.1016/S0883-2927(01)00113-5
901 902 903	Burton, E. A. (1993). Controls on marine carbonate cement mineralogy: review and reassessment. <i>Chemical Geology</i> , <i>105</i> (1–3), 163–179. https://doi.org/10.1016/0009-2541(93)90124-2
904 905 906	Cann, J. R., Blackman, D. K., Smith, D. K., McAllister, E., Janssen, B., Mello, S., et al. (1997). Corrugated slip surfaces formed at ridge–transform intersections on the Mid-Atlantic Ridge. <i>Nature</i> , 385(6614), 329–332. https://doi.org/10.1038/385329a0
907 908 909	Cannat, M., Fontaine, F., & Escartín, J. (2010). Serpentinization and associated hydrogen and methane fluxes at slow-spreading ridges. In <i>Diversity of Hydrothermal Systems on Slow Spreading Ocean Ridges</i> (pp. 241–264). https://doi.org/10.1029/2008GM000760
910 911	Carlson, R. L. (2001). The abundance of ultramafic rocks in Atlantic Ocean crust. <i>Geophysical Journal</i> , <i>144</i> (1), 37–48.
912 913 914 915	<ul> <li>Charlou, J. L., Donval, J. P., Fouquet, Y., Jean-Baptiste, P., &amp; Holm, N. G. (2002).</li> <li>Geochemistry of high H2 and CH4 vent fluids issuing from ultramafic rocks at the Rainbow hydrothermal field (36°14'N, MAR). <i>Chemical Geology</i>, <i>191</i>(4), 345–359. https://doi.org/10.1016/S0009-2541(02)00134-1</li> </ul>
916 917 918 919	Cipolli, F., Gambardella, B., Marini, L., Ottonello, G., & Zuccolini, M. V. (2004). Geochemistry of high-pH waters from serpentinites of the Gruppo di Voltri (Genova, Italy) and reaction path modeling of CO2 sequestration in serpentinite aquifers. <i>Applied Geochemistry</i> , <i>19</i> (5), 787–802. https://doi.org/10.1016/j.apgeochem.2003.10.007
920 921 922	Dabitzias, S. G. (1980). Petrology and Genesis of the Vavdos Cryptocrystalline Magnesite Deposits, Chalkidiki Peninsula, Northern Greece. <i>Economic Geology</i> , 75(8), 1138–1151. https://doi.org/10.2113/gsecongeo.75.8.1138
923 924 925 926	Von Damm, K. L., Bray, A. M., Buttermore, L. G., & Oosting, S. E. (1998). The geochemical controls on vent fluids from the Lucky Strike vent field, Mid-Atlantic Ridge. <i>Earth and</i> <i>Planetary Science Letters</i> , 160(3–4), 521–536. https://doi.org/10.1016/S0012- 821X(98)00108-3
927 928	Deer, W. A., Howie, R. A., & Zussman, J. (1992). Introduction to the Rock-Forming Minerals (2nd ed.). London: Longman.
929 930 931	Detrick, R. S., & Collins, J. A. (1998). Seismic structure of ultramafics exposed at shallow crustal levels in the Mid-Atlantic Ridge rift valley at 15°N. <i>Eos Trans. AGU</i> , 79(45), Fall Meet. Suppl., F800.
932 933 934	Donovan, J. J., & Tingle, T. N. (1996). An Improved Mean Atomic Number Background Correction for Quantitative Microanalysis. <i>Microscopy and Microanalysis</i> , 2(1), 1–7. https://doi.org/10.1017/S1431927696210013
935 936 937	Donovan, J. J., Singer, J. W., & Armstrong, J. T. (2016). A new EPMA method for fast trace element analysis in simple matrices. <i>American Mineralogist</i> , 101(8), 1839–1853. https://doi.org/10.2138/am-2016-5628
938 939	Douville, E., Charlou, J. L., Oelkers, E. H., Bienvenu, P., Jove Colon, C, Donval, J. P., et al. (2002). The rainbow vent fluids (36°14′N, MAR): the influence of ultramafic rocks and

940 941	phase separation on trace metal content in Mid-Atlantic Ridge hydrothermal fluids. <i>Chemical Geology</i> , 184(1–2), 37–48. https://doi.org/10.1016/S0009-2541(01)00351-5
942 943 944	Dromgoole, E. L., & Walter, L. M. (1990). Iron and manganese incorporation into calcite: Effects of growth kinetics, temperature and solution chemistry. <i>Chemical Geology</i> , 81(4), 311–336. https://doi.org/10.1016/0009-2541(90)90053-A
945	Eickmann, B., Bach, W., & Peckmann, J. (2009). Authigenesis of carbonate minerals in modern
946	and Devonian ocean-floor hard rocks. <i>Journal of Geology</i> , <i>117</i> (3), 307–323.
947	https://doi.org/10.1086/597362
948	Eickmann, B., Bach, W., Rosner, M., & Peckmann, J. (2009). Geochemical constraints on the
949	modes of carbonate precipitation in peridotites from the Logatchev Hydrothermal Vent
950	Field and Gakkel Ridge. <i>Chemical Geology</i> , 268(1–2), 97–106.
951	https://doi.org/10.1016/j.chemgeo.2009.08.002
952	Falk, E. S., & Kelemen, P. B. (2015). Geochemistry and petrology of listvenite in the Samail
953	ophiolite, Sultanate of Oman: Complete carbonation of peridotite during ophiolite
954	emplacement. <i>Geochimica et Cosmochimica Acta</i> , 160, 70–90.
955	https://doi.org/10.1016/j.gca.2015.03.014
956 957	Frost, R. B. (1985). On the stability of sulfides, oxides, and native metals in serpentinite. <i>Journal</i> of Petrology, 26(1), 31–63. https://doi.org/10.1093/petrology/26.1.31
958 959	Frost, R. B., & Beard, J. S. (2007). On silica activity and serpentinization. <i>Journal of Petrology</i> , 48(7), 1351–1368. https://doi.org/10.1093/petrology/egm021
960 961 962	Früh-Green, G. L., Kelley, D. S., Bernasconi, S. M., Karson, J. A., Ludwig, K. A., Butterfield, D. A., et al. (2003). 30,000 Years of Hydrothermal Activity at the Lost City Vent Field. <i>Science</i> , 301(5632), 495–498. https://doi.org/10.1126/science.1085582
963	Früh-Green, G. L., Connolly, J. A. D., Plas, A., Kelley, D. S., & Grobéty, B. (2004).
964	Serpentinization of oceanic peridotites: Implications for geochemical cycles and
965	biological activity. In <i>The Subseafloor Biosphere at Mid-Ocean Ridges</i> (pp. 119–136).
966	https://doi.org/10.1029/144GM08
967	Früh-Green, G. L., Orcutt, B. N., Green, S. L., Cotterill, C., Morgan, S., Akizawa, N., et al.
968	(2017). Expedition 357 summary. <i>Proceedings of the International Ocean Discovery</i>
969	<i>Program</i> , 357. https://doi.org/10.14379/iodp.proc.357.101.2017
970	Früh-Green, G. L., Orcutt, B. N., Rouméjon, S., Lilley, M. D., Morono, Y., Cotterill, C., et al.
971	(2018). Magmatism, serpentinization and life: Insights through drilling the Atlantis
972	Massif (IODP Expedition 357). <i>Lithos</i> , 323, 137–155.
973	https://doi.org/10.1016/j.lithos.2018.09.012
974 975 976 977	<ul> <li>Gablina, I. F., Semkova, T. A., Stepanova, T. V., &amp; Gor'kova, N. V. (2006). Diagenetic alterations of copper sulfides in modern ore-bearing sediments of the Logatchev-1 hydrothermal field (Mid-Atlantic Ridge 14°45' N). <i>Lithology and Mineral Resources</i>, <i>41</i>(1), 27–44. https://doi.org/10.1134/S0024490206010032</li> </ul>
978	Gamo, T., Chiba, H., Yamanaka, T., Okudaira, T., Hashimoto, J., Tsuchida, S., et al. (2001).
979	Chemical characteristics of newly discovered black smoker fluids and associated
980	hydrothermal plumes at the Rodriguez Triple Junction, Central Indian Ridge. <i>Earth and</i>

981 982	Planetary Science Letters, 193(3-4), 371-379. https://doi.org/10.1016/S0012-821X(01)00511-8
983 984 985	German, C. R., & Von Damm, K. L. (2003). Hydrothermal Processes. In <i>Treatise on Geochemistry</i> (pp. 181–222). Cambridge: Cambridge University Press. https://doi.org/10.1017/CBO9781139084260.009
986	Giammar, D. E., Bruant, R. G., & Peters, C. A. (2005). Forsterite dissolution and magnesite
987	precipitation at conditions relevant for deep saline aquifer storage and sequestration of
988	carbon dioxide. <i>Chemical Geology</i> , 217(3-4 SPEC. ISS.), 257–276.
989	https://doi.org/10.1016/j.chemgeo.2004.12.013
990	Götze, J. (2012). Application of cathodoluminescence microscopy and spectroscopy in
991	geosciences. <i>Microscopy and Microanalysis</i> , 18(6), 1270–1284.
992	https://doi.org/10.1017/S1431927612001122
993	Greenwood, J., H. (1967). Mineral equilibria in the system MgO-SiO_2-H_2O-CO_2.
994	<i>Researches in Geochemistry</i> , 542–547. Retrieved from
995	http://ci.nii.ac.jp/naid/10004121523/en/
996 997 998	Grozeva, N. G., Klein, F., Seewald, J. S., & Sylva, S. P. (2017). Experimental study of carbonate formation in oceanic peridotite. <i>Geochimica et Cosmochimica Acta</i> , 199, 264–286. https://doi.org/10.1016/j.gca.2016.10.052
999	Hansen, L. D., Dipple, G. M., Gordon, T. M., & Kellett, D. A. (2005). Carbonated serpentinite
1000	(listwanite) at Atlin, British Columbia: A geological analogue to carbon dioxide
1001	sequestration. <i>Canadian Mineralogist</i> , 43(1), 225–239.
1002	https://doi.org/10.2113/gscanmin.43.1.225
1003	Hess, H. H. (1933). The Problem of Serpentinization and the Origin of certain Chrysotile
1004	Asbestos Talc and Soapstone Deposits. <i>Economic Geology</i> , 28, 634–657.
1005	Hövelmann, J., Austrheim, H., Beinlich, A., & Anne Munz, I. (2011). Experimental study of the
1006	carbonation of partially serpentinized and weathered peridotites. <i>Geochimica et</i>
1007	<i>Cosmochimica Acta</i> , 75(22), 6760–6779. https://doi.org/10.1016/j.gca.2011.08.032
1008 1009 1010	Johannes, W. (1967). Zur Bildung und Stabilität von Forsterit, Talk, Serpentin, Quarz und Magnesit im System Mg0-Si02-H20-C02. <i>Contributions to Mineralogy and Petrology</i> , 15, 233–250.
1011	Johannes, W. (1969). An experimental investigation of the system MgO-SiO2-H2O-CO2.
1012	American Journal of Science, 267(9), 1083–1104. https://doi.org/10.2475/ajs.267.9.1083
1013 1014 1015 1016	<ul> <li>Karson, J. A., Früh-Green, G. L., Kelley, D. S., Williams, E. A., Yoerger, D. R., &amp; Jakuba, M. (2006). Detachment shear zone of the Atlantis Massif core complex, Mid-Atlantic Ridge, 30 °n. <i>Geochemistry, Geophysics, Geosystems</i>, 7(6), n/a-n/a. https://doi.org/10.1029/2005GC001109</li> </ul>
1017	Kelemen, P. B., & Matter, J. M. (2008). In situ carbonation of peridotite for CO2 storage.
1018	Proceedings of the National Academy of Sciences of the United States of America,
1019	105(45), 17295–17300. https://doi.org/10.1073/pnas.0805794105
1020	Kelemen, P. B., Matter, J. M., Streit, E. E., Rudge, J. F., Curry, W. B., & Blusztajn, J. S. (2011).
1021	Rates and Mechanisms of Mineral Carbonation in Peridotite: Natural Processes and

1022 1023 1024	Recipes for Enhanced, in situ CO 2 Capture and Storage. <i>Annual Review of Earth and Planetary Sciences</i> , <i>39</i> (1), 545–576. https://doi.org/10.1146/annurev-earth-092010-152509
1025	Kelley, D. S., & Früh-Green, G. L. (2001). Volatile lines of descent in submarine plutonic
1026	environments: Insights from stable isotope and fluid inclusion analyses. <i>Geochimica et</i>
1027	<i>Cosmochimica Acta</i> , 65(19), 3325–3346. https://doi.org/10.1016/S0016-7037(01)00667-
1028	6
1029 1030 1031	<ul> <li>Kelley, D. S., Karson, J. A., Blackman, D. K., Früh-Green, G. L., Butterfield, D. A., Lilley, M. D., et al. (2001). An off-axis hydrothermal vent field near the Mid-Atlantic Ridge at 30 degrees N. <i>Nature</i>, 412(6843), 145–9. https://doi.org/10.1038/35084000</li> </ul>
1032	Kelley, D. S., Karson, J. A., Früh-Green, G. L., Yoerger, D. R., Shank, T. M., Butterfield, D. A.,
1033	et al. (2005). A Serpentinite-Hosted Ecosystem: The Lost City Hydrothermal Field.
1034	<i>Science</i> , 307(5714), 1428–1434. https://doi.org/10.1126/science.1102556
1035	King, H. E., Plümper, O., & Putnis, A. (2010). Effect of secondary phase formation on the
1036	carbonation of olivine. <i>Environmental Science and Technology</i> , 44(16), 6503–6509.
1037	https://doi.org/10.1021/es9038193
1038	Klein, F., & Garrido, C. J. (2011). Thermodynamic constraints on mineral carbonation of
1039	serpentinized peridotite. <i>Lithos</i> , 126(3–4), 147–160.
1040	https://doi.org/10.1016/j.lithos.2011.07.020
1041	Klein, F., & McCollom, T. M. (2013). From serpentinization to carbonation: New insights from
1042	a CO2 injection experiment. <i>Earth and Planetary Science Letters</i> , 379, 137–145.
1043	https://doi.org/10.1016/j.epsl.2013.08.017
1044	Klein, F., Bach, W., & McCollom, T. M. (2013). Compositional controls on hydrogen generation
1045	during serpentinization of ultramafic rocks. <i>Lithos</i> , 178, 55–69.
1046	https://doi.org/10.1016/j.lithos.2013.03.008
1047 1048 1049 1050 1051	<ul> <li>Klein, F., Humphris, S. E., Guo, W., Schubotz, F., Schwarzenbach, E. M., Orsi, W. D., &amp; Karl, D. M. (2015). Fluid mixing and the deep biosphere of a fossil Lost City-type hydrothermal system at the Iberia Margin. <i>Proceedings of the National Academy of Sciences of the United States of America</i>, 112(39), 12036–12041. https://doi.org/10.1073/pnas.1504674112</li> </ul>
1052 1053	Klinkhammer, G., Bender, M., & Weiss, R. F. (1977). Hydrothermal manganese in the Galapagos Rift. <i>Nature</i> , <i>269</i> (5626), 319–320. https://doi.org/10.1038/269319a0
1054	Koons, P. O. (1981). A study of natural and experimental metasomatic assemblages in an
1055	ultramafic-quartzofeldspathic metasomatic system from the Haast schist, South Island,
1056	New Zealand. <i>Contributions to Mineralogy and Petrology</i> , 78(2), 189–195.
1057	https://doi.org/10.1007/BF00373780
1058 1059	Korzhinskii, D. S. (1959). Physicochemical basis of the analysis of the paragenesis of minerals:(English translation], New York, Consultants Bureau. <i>Inc.</i> , 142p.
1060	Kourkoumelis, N. (2013). PowDLL, a reusable .NET component for interconverting powder
1061	diffraction data: Recent developments. In L. O'Neill (Ed.), <i>ICDD Annual Spring</i>
1062	<i>Meetings</i> (Vol. 28, pp. 137–48).

1063 Lafay, R., Montes-Hernandez, G., Janots, E., Chiriac, R., Findling, N., & Toche, F. (2014). 1064 Simultaneous precipitation of magnesite and lizardite from hydrothermal alteration of olivine under high-carbonate alkalinity. Chemical Geology, 368, 63-75. 1065 1066 https://doi.org/10.1016/j.chemgeo.2014.01.008 Lafuente, B., Downs, R. T., Yang, H., & Stone, N. (2015). 1. The power of databases: The 1067 1068 RRUFF project. In T. Armbruster & R. M. Danisi (Eds.), Highlights in Mineralogical Crystallography (pp. 1–30). Berlin, München, Boston: De Gruyter (O). 1069 https://doi.org/10.1515/9783110417104-003 1070 Lilley, M. D., Butterfield, D. A., Lupton, J. E., & Olson, E. J. (2003). Magmatic events can 1071 produce rapid changes in hydrothermal vent chemistry. Nature, 422(6934), 878-881. 1072 1073 https://doi.org/10.1038/nature01569 Lister, C. R. B. (1972). On the thermal balance of a mid-ocean ridge. Geophys. J. R. Astron. 1074 1075 Soc., 26, 515–535. 1076 Ludwig, K. A., Kelley, D. S., Butterfield, D. A., Nelson, B. K., & Früh-Green, G. L. (2006). 1077 Formation and evolution of carbonate chimneys at the Lost City Hydrothermal Field. Geochimica et Cosmochimica Acta, 70(14), 3625–3645. 1078 https://doi.org/10.1016/j.gca.2006.04.016 1079 Ludwig, K. A., Shen, C.-C., Kelley, D. S., Cheng, H., & Edwards, R. L. (2011). U-Th 1080 systematics and 230 Th ages of carbonate chimneys at the Lost City Hydrothermal Field. 1081 1082 Geochimica et Cosmochimica Acta, 75(7), 1869–1888. 1083 https://doi.org/10.1016/j.gca.2011.01.008 Lumsden, D. N., Morrison, J. W., & Lloyd, R. V. (1995). The Role of Iron and Mg / Ca Ratio in 1084 Dolomite Synthesis at 192° C. The Journal of Geology, 103(1), 51-61. 1085 1086 Machel, H. G. (1985). Cathodoluminescence in Calcite and Dolomite and its Chemical 1087 Interpretation. Geoscience Canada, 12(4), 139–147. Malvoisin, B. (2015). Mass transfer in the oceanic lithosphere: Serpentinization is not 1088 isochemical. Earth and Planetary Science Letters, 430, 75-85. 1089 https://doi.org/10.1016/j.epsl.2015.07.043 1090 McCollom, T. M. (2008). Observational, experimental, and theoretical constraints on carbon 1091 1092 cycling in mid-ocean ridge hydrothermal systems. Geophysical Monograph Series, 178, 193-213. https://doi.org/10.1029/178GM10 1093 1094 McCollom, T. M., & Bach, W. (2009). Thermodynamic constraints on hydrogen generation during serpentinization of ultramafic rocks. Geochimica et Cosmochimica Acta, 73(3), 1095 856-875. https://doi.org/10.1016/j.gca.2008.10.032 1096 Mottl, M. J., Holland, H. D., & Corr, R. F. (1979). Chemical exchange during hydrothermal 1097 alteration of basalt by seawater-II. Experimental results for Fe, Mn, and sulfur species. 1098 Geochimica et Cosmochimica Acta, 43(6), 869–884. https://doi.org/10.1016/0016-1099 7037(79)90225-4 1100 1101 Naldrett, A. J. (1966). Tale-carbonate alteration of some serpentinized ultramafic rocks south of 1102 Timmins, Ontario. Journal of Petrology, 7(3), 489–499. https://doi.org/10.1093/petrology/7.3.489 1103

1104 Nooner, S. L., Sasagawa, G. S., Blackman, D. K., & Zumberge, M. A. (2003). Structure of 1105 oceanic core complexes: Constraints from seafloor gravity measurements made at the Atlantis Massif. Geophysical Research Letters, 30(8), 8–11. 1106 1107 https://doi.org/10.1029/2003GL017126 Van Noort, R., Spiers, C. J., Drury, M. R., & Kandianis, M. T. (2013). Peridotite dissolution and 1108 1109 carbonation rates at fracture surfaces under conditions relevant for in situ mineralization 1110 of CO2. Geochimica et Cosmochimica Acta, 106, 1–24. https://doi.org/10.1016/j.gca.2012.12.001 1111 Paukert, A. N., Matter, J. M., Kelemen, P. B., Shock, E. L., & Havig, J. R. (2012). Reaction path 1112 modeling of enhanced in situ CO2 mineralization for carbon sequestration in the 1113 peridotite of the Samail Ophiolite, Sultanate of Oman. Chemical Geology, 330-331, 86-1114 100. https://doi.org/10.1016/j.chemgeo.2012.08.013 1115 1116 Peuble, S., Andreani, M., Godard, M., Gouze, P., Barou, F., Van De Moortele, B., et al. (2015). Carbonate mineralization in percolated olivine aggregates: Linking effects of 1117 crystallographic orientation and fluid flow. American Mineralogist, 100(2-3), 474-482. 1118 1119 https://doi.org/10.2138/am-2015-4913 1120 Peuble, S., Godard, M., Luquot, L., Andreani, M., Martinez, I., & Gouze, P. (2015). CO2 1121 geological storage in olivine rich basaltic aquifers: New insights from reactive-1122 percolation experiments. Applied Geochemistry, 52, 174-190. https://doi.org/10.1016/j.apgeochem.2014.11.024 1123 Picazo, S., Malvoisin, B., Baumgartner, L. P., & Bouvier, A. S. (2020). Low temperature 1124 serpentinite replacement by carbonates during seawater influx in the Newfoundland 1125 margin. Minerals, 10(2). https://doi.org/10.3390/min10020184 1126 Pokrovsky, O. S., & Schott, J. (2002). Surface chemistry and dissolution kinetics of divalent 1127 1128 metal carbonates. Environmental Science and Technology, 36(3), 426–432. 1129 https://doi.org/10.1021/es010925u Proskurowski, G., Lilley, M. D., & Brown, T. A. (2004). Isotopic evidence of magmatism and 1130 seawater bicarbonate removal at the endeavour hydrothermal system. Earth and 1131 Planetary Science Letters, 225(1-2), 53-61. https://doi.org/10.1016/j.epsl.2004.06.007 1132 1133 Proskurowski, G., Lilley, M. D., Kelley, D. S., & Olson, E. J. (2006). Low temperature volatile production at the Lost City Hydrothermal Field, evidence from a hydrogen stable isotope 1134 1135 geothermometer. Chemical Geology, 229(4), 331-343. https://doi.org/10.1016/j.chemgeo.2005.11.005 1136 Proskurowski, G., Lilley, M. D., Seewald, J. S., Früh-Green, G. L., Olson, E. J., Lupton, J. E., et 1137 al. (2008). Abiogenic Hydrocarbon Production at Lost City Hydrothermal Field. Science, 1138 319(5863), 604-607. https://doi.org/10.1126/science.1151194 1139 Robinson, P. T., Malpas, J., Zhou, M. F., Ash, C., Yang, J. S., & Bai, W. J. (2005). 1140 Geochemistry and Origin of Listwanites in the Sartohay and Luobusa Ophiolites, China. 1141 1142 International Geology Review, 47(2), 177–202. https://doi.org/10.2747/0020-6814.47.2.177 1143

1144 1145 1146	Rouméjon, S., & Cannat, M. (2014). Serpentinization of mantle-derived peridotites at mid-ocean ridges: Mesh texture development in the context of tectonic exhumation. <i>Geochemistry, Geophysics, Geosystems</i> , 15(6), 2354–2379. https://doi.org/10.1002/2013GC005148
1147	Rouméjon, S., Früh-Green, G. L., Orcutt, B. N., & IODP Expedition 357 Science Party. (2018).
1148	Alteration heterogeneities in peridotites exhumed on the southern wall of the Atlantis
1149	Massif (IODP Expedition 357). <i>Journal of Petrology</i> , 59(7), 1329–1358.
1150	https://doi.org/10.1093/petrology/egy065
1151	Rouméjon, S., Williams, M. J., & Früh-Green, G. L. (2018). In-situ oxygen isotope analyses in
1152	serpentine minerals: Constraints on serpentinization during tectonic exhumation at slow-
1153	and ultraslow-spreading ridges. <i>Lithos</i> , 323, 156–173.
1154	https://doi.org/10.1016/j.lithos.2018.09.021
1155	Schandl, E. S., & Naldrett, A. J. (1992). CO2 metasomatism of serpentinites, south of Timmins,
1156	Ontario. <i>Canadian Mineralogist</i> , <i>30</i> , 93–108. Retrieved from
1157	http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.558.3377&rep=rep1&type=pdf
1158	Schandl, E. S., & Wicks, F. J. (1991). Two stages of CO2 metasomatism at the Munro mine,
1159	Munro Township, Ontario: evidence from fluid-inclusion, stable-isotope, and
1160	mineralogical studies. <i>Canadian Journal of Earth Sciences</i> , 28(5), 721–728.
1161	https://doi.org/10.1139/e91-062
1162	Schott, J., Pokrovsky, O. S., & Oelkers, E. H. (2009). The link between mineral
1163	dissolution/precipitation kinetics and solution chemistry. <i>Reviews in Mineralogy and</i>
1164	<i>Geochemistry</i> , 70, 207–258. https://doi.org/10.2138/rmg.2009.70.6
1165	Schroeder, T. J., & John, B. E. (2004). Strain localization on an oceanic detachment fault system,
1166	Atlantis Massif, 30°N, Mid-Atlantic Ridge. <i>Geochemistry, Geophysics, Geosystems</i> ,
1167	5(11). https://doi.org/10.1029/2004GC000728
1168	Schroeder, T. J., John, B. E., & Frost, R. B. (2002). Geologic implications of seawater
1169	circulation through peridotite exposed at slow-spreading mid-ocean ridges. <i>Geology</i> ,
1170	30(4), 367–370.
1171	Schroeder, T. J., Bach, W., Jöns, N., Jöns, S., Monien, P., & Klügel, A. (2015). Fluid circulation
1172	and carbonate vein precipitation in the footwall of an oceanic core complex, Ocean
1173	Drilling Program Site 175, Mid-Atlantic Ridge. <i>Geochemistry, Geophysics, Geosystems</i> ,
1174	16(10), 3716–3732. https://doi.org/10.1002/2015GC006041
1175	Schwarzenbach, E. M., Früh-Green, G. L., Bernasconi, S. M., Alt, J. C., & Plas, A. (2013).
1176	Serpentinization and carbon sequestration: A study of two ancient peridotite-hosted
1177	hydrothermal systems. <i>Chemical Geology</i> , 351, 115–133.
1178	https://doi.org/10.1016/j.chemgeo.2013.05.016
1179	Schwarzenbach, E. M., Lang, S. Q., Früh-Green, G. L., Lilley, M. D., Bernasconi, S. M., &
1180	Méhay, S. (2013). Sources and cycling of carbon in continental, serpentinite-hosted
1181	alkaline springs in the Voltri Massif, Italy. <i>Lithos</i> , 177, 226–244.
1182	https://doi.org/10.1016/j.lithos.2013.07.009
1183 1184	Schwarzenbach, E. M., Gill, B. C., Gazel, E., & Madrigal, P. (2016). Sulfur and carbon geochemistry of the Santa Elena peridotites: Comparing oceanic and continental

1185	processes during peridotite alteration. <i>Lithos</i> , 252–253, 92–108.
1186	https://doi.org/10.1016/j.lithos.2016.02.017
1187	Seifritz, W. (1990). CO2 disposal by means of silicates. Nature, 345(June), 1990.
1188	Seyfried, W. E., Pester, N. J., Tutolo, B. M., & Ding, K. (2015). The Lost City hydrothermal
1189	system: Constraints imposed by vent fluid chemistry and reaction path models on
1190	subseafloor heat and mass transfer processes. <i>Geochimica et Cosmochimica Acta</i> , 163,
1191	59–79. https://doi.org/10.1016/j.gca.2015.04.040
1192	Spandler, C., Hermann, J., Faure, K., Mavrogenes, J. A., & Arculus, R. J. (2008). The
1193	importance of talc and chlorite "hybrid" rocks for volatile recycling through subduction
1194	zones; evidence from the high-pressure subduction mélange of New Caledonia.
1195	<i>Contributions to Mineralogy and Petrology</i> , 155(2), 181–198.
1196	https://doi.org/10.1007/s00410-007-0236-2
1197	Trommsdorff, V., & Evans, B. W. (1977). Antigorite-ophicarbonates: Phase relations in a
1198	portion of the system CaO-MgO-SiO2-H2O-CO2. <i>Contributions to Mineralogy and</i>
1199	<i>Petrology</i> , 60(1), 39–56. https://doi.org/10.1007/BF00372850
1200	Ulrich, M., Muñoz, M., Guillot, S., Cathelineau, M., Picard, C., Quesnel, B., et al. (2014).
1201	Dissolution-precipitation processes governing the carbonation and silicification of the
1202	serpentinite sole of the New Caledonia ophiolite. <i>Contributions to Mineralogy and</i>
1203	<i>Petrology</i> , 167(1), 1–19. https://doi.org/10.1007/s00410-013-0952-8
1204	Wetzel, L. R., & Shock, E. L. (2000). Distinguishing ultramafic-from basalt-hosted submarine
1205	hydrothermal systems by comparing calculated vent fluid compositions. <i>Journal of</i>
1206	<i>Geophysical Research: Solid Earth</i> , 105(B4), 8319–8340.
1207	https://doi.org/10.1029/1999jb900382
1208 1209	Wheat, C. G., & Mottl, M. J. (2004). Geochemical fluxes through mid-ocean ridge flanks. <i>In Hydrogeology of the Oceanic Lithosphere</i> , 627–658.