Distribution and Sources of Carbon in Serpentinized Mantle Peridotites at the Atlantis Massif (IODP Expedition 357)

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Abstract The carbon geochemistry of serpentinized peridotites and gabbroic rocks recovered during IODP Expedition 357 on the Atlantis Massif (AM) was examined to characterize carbon sources and the fate of dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) in seawater during long-lived hydrothermal circulation and serpentinization. Carbon isotopes reveal three stages of carbonate formation, starting at least 38,000 yr ago: (a) Early dispersed carbonate precipitation, with low water/rock ratios and high temperatures (50°C–190°C); (b) carbonate vein formation related to high and focused fluid fluxes still at high temperatures (30°C–200°C); and (c) seawater circulation leading to cold carbonate precipitation controlled by late, brittle fractures during uplift, and unroofing of the oceanic core complex. Our study reveals three main DIC sources in the system: (a) DIC from abiotic hydrothermal degradation of dissolved organic matter (OM); (b) DIC from seawater; and (c) DIC from mantle-derived volatiles. Basement rocks containing dispersed carbonates are characterized by high concentrations (~800 ppm) of total non-carbonate carbon (NCC) and 13C-depleted carbonates. We propose that high seawater fluxes in the southern part of the AM likely favor the transport and incorporation of marine DOC in serpentinites and that carbonates record isotopic signals of OM decay. Our study indicates that organic carbon accounts for a significant proportion of the total carbon stored in the AM and suggests that serpentinites may be an important sink of DOC from seawater.

Plain Language Summary Carbon can be found in higher concentrations within the atmosphere, terrestrial biosphere, oceans, and lithosphere. It is an essential element for various abiotic and biotic reactions and is in the form of CO2 and CH4, an important greenhouse gas. The transfer of carbon between different reservoirs is not well constrained. This study uses samples recovered by drilling the lithosphere at the Atlantis Massif (AM) and chemical investigations to evaluate carbon sources, speciation, and transformations. The AM is located in the Atlantic Ocean close to the Mid-Atlantic-Ridge and comprises a high amount of mantle rocks exposed at the seafloor. Mantle rocks react in contact with water to form serpentine and create an environment that promotes the transformation of CO2 into carbonates. Our results demonstrate that the oceanic lithosphere is a significant reservoir of organic compounds and inorganic carbonates and that carbonates record the oxidation of organic matter over long periods. Our study can help to evaluate the potential of mantle rocks to store carbon and reduce CO2 emission. However, it may also provide information to evaluate the potential for life within the lithosphere, not only on Earth but also on other planets where serpentinization processes occur.

1. Introduction

Hydrothermal circulation of seawater through the oceanic crust occurs at such rates that the entire volume of the ocean may be cycled through the oceanic crust in less than 20 Myr (German & Von Damm, 2003; Wheat & Mottl, 2004). This high fluid flux, coupled with extensive fluid-rock interaction, has significant consequences for the thermal structure and rheology of the oceanic lithosphere, geochemical budgets of the ocean, and microbial processes within and at the seafloor (e.g., Kelley & Früh-Green, 2001; Lister, 1972; Proskurowski et al., 2006; Wheat & Mottl, 2004). At slow-spreading ridges, hydrated upper mantle rocks (serpentinites) are commonly exposed at the seafloor and constitute highly reactive chemical and thermal systems. Carbon—one of the most important elements on Earth—is stored within the lithosphere in the form of gaseous CO2 and CH4 within mineral inclusions or as solid phases, such as carbonate and graphite, and organic compounds. These may persist in ancient mantle domains over extended periods of time.
Previous studies have shown that the speciation, concentration, and isotopic composition of carbon in serpentinites can be used to gain information about the chemical and physical conditions of the reservoir and the dominant physical, chemical, and/or biological processes in the system (Charlou et al., 2002; Delacour, Früh-Green, Bernasconi, & Kelley, 2008; Kelley et al., 2005; Schwarzenbach et al., 2013; Shanks et al., 1995).

Recent studies provide evidence that microbial life may be sustained within the lithosphere by fluid-mediated chemical reactions that provide utilizable energy resources, implying that the deep subsurface biosphere may be the largest microbial habitat on Earth (Barry et al., 2019; Colman et al., 2017; Fullerton et al., 2019). For example, redox reactions during the formation of serpentine from mantle olivine and pyroxene generate substantial amounts of H₂ (Barnes et al., 1972; Barnes & O’Neil, 1969; McCollom & Bach, 2009; Neal & Stanger, 1983; Thayer, 1966), and may promote abiotic synthesis of CH₄ (Abrajano et al., 1990; Charlou et al., 2010; Etiope & Sherwood Lollar, 2013; McCollom, 2013; Szatmari, 1989; Welhan, 1988). Production of H₂ and CH₄ by serpentinization of mantle rocks has been identified at mid-ocean ridges (Cannat et al., 2010; Kelley et al., 2005; Konn et al., 2015; Welhan & Craig, 1979), as well as on-land (Etiope & Sherwood Lollar, 2013) and in the shallow forearc of subduction zones (Mottl et al., 2003; Ohara et al., 2012). Although serpentinization reactions can lead to the production of fluids with high pH ranging from 9 to 11, depending on temperature, which may limit nutrient and electron acceptor availability (Schrenk et al., 2013), metagenomic studies of serpentinization-fueled, hydrothermal deep-sea vents, and continental fluid seeps provide evidence for microbial H₂ and CH₄ utilization (Brazelton et al., 2012; Curtis et al., 2013; Ohara et al., 2012; Schrenk et al., 2013).

Hydration of mantle peridotites can also be associated with large carbonate deposits. Serpentinization at temperatures below ~200°C–250°C produces fluids with high Ca²⁺ concentration and high pH, which can cause carbonate precipitation (e.g., Frost & Beard, 2007; Neal & Stanger, 1985; Palandri & Reed, 2004). Recently, carbonate formation from ultramafic rocks has received considerable attention as a potential means to sequester atmospheric CO₂ and reduce global warming (Boschi et al., 2017; Kelemen et al., 2011; Seifritz, 1990). Previous studies indicate that 5%–9% of the rocks exposed along slow- and ultraslow-spreading MOR consist of hydrothermally altered peridotite (Cannat et al., 2010; Carlson, 2001) and Kelemen and Matter (2008) argue that mantle peridotites exposed on land have a high capacity to sequester CO₂. This makes serpentinites a significant but still poorly quantified sink for dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC). However, many findings of hydrothermal carbon species are based on experimental studies of fluids (e.g., Seewald, 2001), and only a few studies are available on the geochemistry of organic (Alt et al., 2012; Delacour, Früh-Green, Bernasconi, Schaeffer, & Kelley, 2008; Früh-Green et al., 2004; Kelley & Früh-Green, 1999) and inorganic carbon in oceanic peridotites (Bach et al., 2011; Coggon et al., 2004; Delacour, Früh-Green, Bernasconi, Schaeffer, & Kelley, 2008; Eickmann et al., 2009; Klein et al., 2013; Schwarzenbach et al., 2013). It remains unclear how and to what extent hydration processes in the upper mantle affect the global carbon cycle on different geological time scales. To address these questions, a better understanding of the fate of carbon within these systems is needed.

Here, we present a study of carbon and oxygen isotope geochemistry of basement rocks of the Atlantis Massif (AM) close to the Lost City Hydrothermal Field (LCHF) that were recovered during International Ocean Discovery Program (IODP) Expedition 357 (Früh-Green et al., 2017b). The LCHF, located on the southern wall of the AM, is an end-member for serpentinite-hosted, hydrothermally active systems at the slow-spreading Mid-Atlantic Ridge (MAR) and serves as an excellent present-day analog for fossil serpentine-hosted hydrothermal systems (e.g., Chenaillot Ophiolite, Lafay et al., 2017; Northern Apennine ophiolites, Barbieri, et al., 1979). It is an off-axis, low-temperature, peridotite-dominated system driven by migration of seawater along deeply penetrating fault systems that leads to hydration and serpentinization of the upper mantle. The LCHF offers a unique opportunity to study the interplay of serpentinization, deformation, and transformation of carbon during unroofing and uplift of the AM and the impact these processes have on habitability for microorganisms. This information helps to better understand the fate of carbon in marine hydrothermal systems and provides constraints on the thermal evolution of the AM. Our study aims at characterizing biogenic and abiotic processes controlling carbon cycling within the oceanic lithosphere. Recent studies indicate that serpentinization reactions have also likely occurred on Mars and beneath icy oceans on Saturn’s moon Enceladus and Jupiter’s moon Europa (Ehlmann et al., 2010; Glein.
et al., 2015; Jones et al., 2018; Sekine et al., 2015). Thus, our research is relevant to understand serpentinizing processes on Earth and other terrestrial bodies in the Solar System.

Below we present detailed geochemical analyses of the inorganic and organic carbon together with radiocarbon ages of the basement rocks of the AM. This data allows us to unravel the complexity of this unique system and discuss the sources and speciation of carbon and the critical roles that fluids and deformation play in regulating long-term storage and global carbon cycling within the hydrated and serpentinized oceanic lithosphere.

2. Geological Setting and Sampling

The AM, located at 30°N along the slow-spreading MAR, is a 1.5–2 Myr old, dome-like massif forming the inside corner of the intersection between the MAR and the Atlantis Transform Fault (ATF; Figure 1). The massif is interpreted as an oceanic core complex (OCC), comprised of lower crustal and upper mantle rocks that were uplifted and exposed by long-lived, low-angle detachment faulting (Blackman et al., 1998, 2002; Cann et al., 1997; Karson et al., 2006). Three lithologic domains can be distinguished: the corrugated central 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 part of the Southern Ridge and defines the edge of the ATF; and the basaltic eastern block, which 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 covered by pelagic sediments, rubble, and sedimentary breccias (Blackman et al., 2002; Boschi et al., 2006; Früh-Green et al., 2003; Karson et al., 2006; Schroeder et al., 2002).

The LCHF is located on a fault-bounded terrace just below the top of the southern wall near the summit. It is composed of numerous active and inactive, up to 60 m tall, carbonate-brucite chimneys, which vent low-temperature (40°C–95°C), alkaline (pH 9–11) fluids (Kelley et al., 2001, 2005; Lang et al., 2010; Ludwig et al., 2006; Seyfried et al., 2015). The vent fluids are characterized by low silica, metal, and CO₂ concentrations and high H₂ (up to 15 mmol/kg), CH₄ (1–2 mmol/kg), Ca (~30 mmol/kg), formate (36–158 μmol/kg), acetate (1–35 μmol/kg), and low-molecular-weight hydrocarbons concentrations. The high concentrations of molecular hydrogen, methane, and formate could provide metabolic energy for microbes (Lang et al., 2012; McCollom & Seewald, 2007). Recent genetic sequencing efforts demonstrated that the active carbonate chimney structures at Lost City host microbial communities dominated by archaeal Methanosarcinaceae (LCMS) with lower proportions of different bacteria strains (Brazelton et al., 2006; Schrenk et al., 2004). Three important metabolic reactions in the Lost City chimneys have been proposed: sulfate reduction, methanogenesis, and anaerobic methane oxidation (Brazelton et al., 2006; Kelley et al., 2005; Lang et al., 2018; Orcutt et al., 2011; Schrenk et al., 2004). Hydrothermal circulation is believed to be driven by residual crustal heat and lithospheric cooling, with the composition of the fluids controlled by subsurface serpentinization reactions in the underlying mantle rock. Based on radiocarbon dating, hydrothermal activity has been active for at least 30,000 yr (Früh-Green et al., 2003; Kelley et al., 2005), and subsequent U-Th analyses indicated that this is a minimum age as some of the carbonate deposits yielded ages of up to 120,000 yr (Ludwig et al., 2011).

2.1. IODP Expedition 357

IODP Expedition 357 drilled 17 shallow boreholes (from 1.3 mbsf [meters below seafloor] to maximum 16.4 mbsf) at nine sites along an east-west transect across the AM (Figure 1). Two sites are on the eastern end of the southern wall (Sites M0068 and M0075), three in the central section north of the LCHF (Sites M0069, M0072, and M0076), two on the western end (Sites M0071 and M0073), and two sites are to the north in the direction of the central dome and IODP Site U1309 (Sites M0070 and M0074). The recovered mafic and ultramafic rocks reveal a high and heterogeneous degree of serpentinization and metasomatic talc-amphibole-chlorite overprinting and local rodingitization (Früh-Green et al., 2017b, 2018). Contacts between ultramafic and gabbroic rocks are marked by silica metasomatism with talc, tremolite, and chlorite (Holes M0068B, M0072B, and M0076B) in part replacing pyroxenes. This indicates that hydration may have started at temperatures in the range of 400°C–500°C and that orthopyroxene alteration pre-dates the onset
of serpentinization of olivine (Rouméjon, Früh-Green, et al., 2018; Schroeder & John, 2004). Field and geophysical studies estimate that at least ~20% of the massif is completely serpentinized (Detrick & Collins, 1998; Früh-Green et al., 2003; Nooner et al., 2003). Two main stages of hydration can be distinguished: an initial stage of pervasive serpentinization at temperatures of 200°C–350°C (Boschi et al., 2008; Rouméjon, Früh-Green, et al., 2018; Rouméjon, Williams, et al., 2018) followed by a second stage dominated by focused fluid flow and leading to serpentine recrystallization and vein formation dominated by chrysotile or antigorite (Rouméjon, Früh-Green, et al., 2018).

This study focuses mainly on the five sites containing altered peridotite (Sites M0068, M0069, M0070, M0071, M0072, M0073, M0074, M0075, and M0076, Figure 2). The four remaining sites include foraminifera-bearing carbonate ooze, rubble blocks of variable lithologies, and sedimentary breccia with volcanic clasts and carbonate sediments (Früh-Green et al., 2017b). The studied sites had a core recovery rate ranging between 30% (Hole M0071C) and 75% (Hole M0069A), with an average recovery rate of 58%. Drill cores of IODP Expedition 357 are described.
in detail in (Früh-Green et al. (2017b), Früh-Green et al. (2018, Supporting Information), and Rouméjon, Früh-Green, et al. (2018, Supporting Information).

3. Analytical Methods

Isotopic investigations from 8 sites (15 holes) of Expedition 357, covering the diversity of rock types and alteration textures, included 69 peridotites (42 harzburgites, 19 dunites, and 8 serpentinite rubble samples), 33 mafic rocks (9 gabroic rocks, 13 doleritic rocks), and 11 talc-amphibole ± chlorite schists. Furthermore, we measured clumped isotopes on 28 carbonate veins from 16 serpentinized peridotites. Sample locations are shown in Figure 2, together with a simplified lithostratigraphy and location of identified carbonate features.

By IODP convention, the cored interval is measured in mbsf determined while drilling. The recovered cores are cut into sections with a maximum length of 1.5 m and numbered sequentially from the top. The curated depth of a sample is calculated by adding the depth of the sample below the section top and the lengths of all higher sections in the core to the core-top datum measured with the drill rods (see Expedition 357 methods in Früh-Green et al., 2017a). When the recovered core is shorter than the cored interval, the top of the core, by convention, is equated to the top of the cored interval. A full identification number for a sample is defined by IODP guidelines as: Expedition_Drilling-Platform, Site, Hole_Core, Coretype_Section_Interval in cm (e.g., 357_M0076B_9R_1_5–9). For simplicity, we have removed the expedition and drilling platform information which is the same for all samples (e.g., 76B_9R_1_5–9 is a shortened version of the sample above taken from Site M0076, core 9R during Exp. 357).
3.1. Sample Preparation and Sample Fractions

Sample preparation depended on whether the samples were collected under sterile conditions for microbiological studies (denoted as MBio samples) or whether the samples were obtained using standard IODP protocols (denoted as standard IODP samples). Onboard ship, the MBio samples were immediately wrapped in acid-washed and autoclaved Teflon sheeting, frozen at −80°C in Whirl-Pak bags, and shipped frozen for further processing and subsampling at the Kochi Core Center Kochi University/JAMSTEC, Shikoku, Japan. There, the outsides of the frozen pieces of cores were carefully removed and subsampled while still frozen under clean air conditions and subsequently distributed for interlaboratory analyses. MBio_TIC denotes subsamples in which the internal material was crushed and homogenized using solvent-cleaned equipment, then wrapped in sterile Teflon sheeting and frozen at −20°C. Subsamples denoted as MBio_xTIC were rinsed 10 times in Milli-Q water before crushing and homogenization. A description of sample handling procedures during Expedition 357 can be found in the Expedition 357 methods in Früh-Green et al. (2017a). Because the MBio samples were already powdered or were pebbles collected from the cores, they could not be used for macro- or microscopic observations. Photographs of the archive half and descriptions of the remaining cores made during the Expedition 357 sampling party provide a rough lithological and structural context for the MBio samples (Früh-Green et al., 2017b, 2018, Supporting Information).

The standard IODP samples are cut rock slabs or pebbles collected from the cores during the Exp. 357 onshore science party (Früh-Green et al., 2017b). In our laboratory, the samples were cleaned by ultrasonication in 100 ml dichloromethane (DCM) for 5 min at room temperature and subsequently dried for 24 h at room temperature in a pre-combusted glass container covered with combusted aluminum foil. This cleaning step was not performed on the MBio powdered samples. The MBio samples and the cleaned rocks slabs from standard IODP samples were then crushed, centerpiece collected, and ground by hand using an agate mortar cleaned with DCM to obtain a homogenous powder.

We conducted whole-rock analyses to determine concentrations of total carbon (TC), total inorganic carbon (TIC), and total non-carbonate carbon (NCC), and the isotopic compositions (δ13C and δ18O) of TIC, total carbon (δ13C_C), and total non-carbonate (acid-insoluble) carbon (δ13C_NCC). TIC represents all inorganic carbon from a whole-rock powder (including potential carbonate veins) that reacts at room temperature within 24 h with 3M hydrochloric acid (HCl). Total NCC represents all remaining acid-insoluble carbon phases, which can include organic compounds, amorphous carbon, graphite, etc.; this carbon fraction is commonly reported collectively as total organic carbon (TOC; e.g., Delacour, Früh-Green, Bernasconi, Schaeffer, & Kelley, 2008). Previously reported organic compounds within the central dome of the AM are pristane, phytane, and squalene, and polycyclic compounds and n-C14 to n-C30 alkane were found in surface samples (Delacour, Früh-Green, Bernasconi, Schaeffer, & Kelley, 2008). Based on Raman microspectroscopy (LabRAM HR Evolution UV-VIS-NIR; Horiba, Kyoto, Japan) on selected samples with high NCC content (Site M0072), the presence of disordered carbonaceous matter is evident by first-order D-bands in fully serpentinized olivine. The spectrum of organic material in this order is characterized by two main bands; the graphitic (G) band, which occurs at ~1,600 cm⁻¹; and the disordered (D) band, which occurs ~1,350 cm⁻¹ (Beyssac et al., 2003). We propose that organic compounds are the predominant constituent of the NCC in our study, but we cannot rule out the presence of amorphous carbon or graphite and therefore prefer not to use the term TOC.

The NCC and δ13C_NCC were determined on 200 mg aliquots decarbonated with 3 ml of 3M HCl. The remaining material was rinsed several times with Milli-Q water, dried at 70°C overnight, and re-homogenized by hand using an agate mortar before analysis. For clumped isotope analyses and radiocarbon dating, 28 carbonate veins with a thickness of more than 0.5 mm were selected. In a first step, the standard IODP samples were cleaned with 2-propanol and compressed air. Later, the surfaces of the veins were removed and discarded, followed by sampling of the veins with a hand-held drill. The obtained vein material was, in a second step, homogenized using an agate mortar.

3.2. Powder X-Ray Diffraction

Crystallographic analyses were made using a Bruker AXS D8 Advance Powder X-ray Diffractometer (XRD) equipped with a Lynxeye superspeed detector (Bruker Corporation, Billerica, MA, USA) with Cu-Kα
radiation at a voltage of 45 kV and a current of 40 mA, with 2θ ranging between 10° and 60° with a step size of 0.01°, and measurement time of 1 s per step. Quantification of the mineralogy was carried out using the program PowDII (Kourkoumelis, 2013) and the RRUFF database (Lafuente et al., 2015).

3.3. Carbon Content and Isotopic Composition

TC and NCC contents and isotopic compositions were determined by combustion of 1–60 mg of sample using a FlashEA 1112 Elemental Analyzer (EA) interfaced via a ConFlo IV to a Delta V Plus Isotope Ratio Mass Spectrometer (MS; all Thermo Fisher Scientific, Bremen, Germany). The carbon content was calculated using two standards (Bodenstandards No. 5; 0.141%C, HEKAtch, Wegberg, Germany, and nicotinamide; 59.01%C, Thermo Fisher Scientific, Milan, Italy). Empty tin capsules were measured for blank correction. Analytical reproducibility of δ13C_TC and δ13C_NCC is ±0.11‰ (1σ). The detection limit for a reproducible carbon isotope measurement is about 1 μg C.

TIC contents were either measured on a CM 5012 CO2 coulometer interfaced with a CM 5130 Acidification Module or were calculated by subtraction of total NCC content from TC or by mass balance using Equation 1.

\[
\left( f_{\text{TC}} \times \delta^{13}C_{\text{TC}} \right) = \left( f_{\text{HCl}} \times \delta^{13}C_{\text{TIC}} \right) + \left( f_{\text{NCC}} \times \delta^{13}C_{\text{NCC}} \right)
\]  

For coulometric measurements, 20–30 mg of sample was weighed into glass capsules and reacted with 2M perchloric acid (HClO4). Precision depended on the TIC content and was determined from internal laboratory standards and replicate analyses. Reproducibility for TIC is better than 2.5% for standards with more than 1 wt% carbon, and the maximum error for <600 ppm carbon is ±30 ppm (see Schwarzenbach et al., 2013).

δ13C and δ18O of TIC were measured on a GasBench II connected to a Delta V Mass Spectrometer (both Thermo Fisher Scientific, Bremen, Germany), as described in detail in Breitenbach and Bernasconi (2011). The average long term reproducibility based on replicate standards is ±0.10‰ for δ13C and ±0.11‰ for δ18O (1σ) for samples containing more than 20 μg carbonate, which are reported as replicates. Samples with lower TIC concentration are reported as individual measurements with a conservatively estimated larger uncertainty of ±1‰. The instrument was calibrated with the international standards NBS19 (δ13C = 1.95‰ and δ18O = −2.2‰) and NBS18 (δ13C = −5.01‰ and δ18O = −23.01‰). A subset of carbonate veins was analyzed for clumped isotopes (Δ47) on a Kiel IV carbonate device interfaced with a Thermo Fisher Scientific MAT253 isotope ratio mass spectrometer following the methodology described in detail in Meckler et al. (2014) and Müller et al. (2017). Briefly, 100–110 μg of carbonate were reacted with three drops of 104% phosphoric acid (H3PO4) at 70°C. The evolved CO2 was purified on a custom-built Porapak Q trap held at −40°C and measured on a MAT253 in micro-volume mode using the long-integration dual-inlet (LIDI) Protocol (Hu et al., 2014; Müller et al., 2017). The results are converted to the Carbon Dioxide Equilibrium Scale (CDES) using the carbonate standards ETH-1, ETH-2, and ETH-3 as described in Bernasconi et al. (2018). Dolomite values are reported for a reaction temperature of 70°C, which is the same temperature used to establish the calibration (Müller et al., 2019), and calcites are projected to 25°C. With a reasonable amount of replicate analyses, the margins of error are ±3°C–5°C at the 95% CL (Fernández et al., 2017). However, due to the limited amount of available material, the number of replicate measurements was limited and varied between 1 and 12; thus, precision could not always be reached. δ13C and δ18O of TIC and δ13C of TC and NCC are reported in conventional delta notation with respect to the Vienna Pee Dee Belemnite (VPDB) standard. Clumped isotopes allow the calculation of δ18O of the fluid in equilibrium with the carbonate vein. We used the calibration of Grossman and Ku (1986) for aragonite, O’Neil et al. (1969) corrected by Friedman & O’Neil (1977) for calcites, and Müller et al. (2019) for dolomites. The uncertainty for the calculated δ18O of the water depends on the number of replicate measurements.

3.4. Radiocarbon Ages

Radiocarbon ages of whole-rock and decarbonated samples were measured by combustion with an Elemental Analyzer interfaced to a MICADAS accelerator mass spectrometer (AMS; Synal et al., 2007) equipped
with gas-ion source at the Laboratory of Ion Beam Physics, ETH Zurich, and detailed methods are reported in Ruff et al. (2010) and Wacker et al. (2010). Carbonate veins were measured by placing them in vacutainers which were purged for 10 min with He and converted to CO$_2$ through the addition of 85% H$_3$PO$_4$, followed by direct injection of the gas into the ion source of the AMS. The results are normalized against standard Oxalic Acid II (NIST SRM 4990C) and corrected with a radiocarbon blank CO$_2$ (IAEA C-1). In addition, IAEA-C2 and coral CSTD were measured in each run to test the accuracy of the measurement. The precision was better than ±5‰ on a modern standard. Radiocarbon data are expressed as F$^{14}$C (fraction of modern carbon) and conventional $^{14}$C ages, according to Reimer et al. (2004).

4. Results

Five sites with altered peridotites (Sites M0071, M0072, M0069, M0076, and M0068) make up the focus of this study and can be divided into two groups. The northwestern (M0071) and most eastern sites (M0068) contain varying proportions of ultramafic, mafic, and sedimentary rocks that have been interpreted as originating from mass-wasting and local faulting processes (Früh-Green et al., 2017b; Rouméméon, Früh-Green, et al., 2018). These holes can be used to interpret the general alteration history of the AM but should be considered with caution for more detailed and depth-dependent interpretations. The sites from the central part of the southern wall (M0072, M0069, and M0076) are considered in situ portions of the AM indicated by coherent, decimeter- to meter-long sections of cores, as well as consistent structural measurements (Früh-Green et al., 2017b, 2018).

Carbonates in the mantle rocks of the AM occur as veins, as a replacement of serpentinized olivine, and as finely dispersed grains. Veins are the most abundant carbonate occurrence and tend to be concentrated in the serpentinites from the central drill sites closest to the LCHF (M0069, M0072, and M0076; Figure 2). The veins are composed of magnesite, dolomite, calcite, and aragonite in variable proportions. Magnesite veins are the least frequent, occurring exclusively in association with dolomite and limited to the deeper sections of Hole M0076B (>12 mbsf). The most abundant and volumetrically dominant vein-type are up to 1 cm wide aragonite veins that are observed throughout the ultramafic rocks at Hole M0069A, in the deeper section of Hole M0076B (>13 mbsf), in the top cores from Holes M0071A and M0068B, and on the altered surface of a deeper sample from Hole M0068B (Figure 2). The aragonite veins crosscut the primary rock fabric and postdate all secondary fabrics, indicating they are the last to have formed.

4.1. Carbon Geochemistry

Comparing results from the sterile MBio rocks samples (rinsed and non-rinsed) with samples collected with regular IODP sampling protocol offers the possibility to evaluate possible procedural contaminations (Figure 3). Considering the natural heterogeneities of the rocks, samples with TC > 0.1 wt% show similar concentrations and isotopic compositions, independent of the handling procedure. Samples with TC < 0.1 wt% show minor variations, whereby the MBio sample sets show no difference between each other but tend to have less TC than the standard IODP samples but still within the range of error. No noticeable differences are seen in TIC and NCC contents and isotopic compositions related to handling protocols.

4.1.1. Basement Rocks

Carbon contents and isotope compositions are given in Table 1. The basement rocks show a wide range of TC varying from 48 ppm to 5 wt% and $\delta^{14}$C$_{TC}$ values from −26.3‰ to +1.4‰. The majority of the samples have less than 0.2 wt% TC (see Figure 4). Gabbroic rocks and talc-amphibole chlorite schists have less variable TC contents with an average concentration below 202 ppm and a maximum of 801 ppm. The TC in serpentinites ranges from 80 ppm to 4.9 wt%, with the higher concentrations observed in the upper 0.7 mbsf at Hole M0071A, in the deeper parts of Holes M0069A and M0072B, and throughout Hole M0076B. Variations in $\delta^{13}$C$_{TC}$ mainly reflect variations in carbonate contents. The majority of the mafic rocks have TIC contents below 123 ppm and $\delta^{13}$C$_{TC}$ values from −12.5‰ to −6.4‰ (Figures 3a and 3b). The serpentinites show TIC content ranging from below detection limit to 5.0 wt% with $\delta^{13}$C$_{TC}$ ranging between −11.6‰ and + 2.4‰. Most serpentinites with TIC above 500 ppm have average $\delta^{13}$C$_{TC}$ values of +1.1‰, which is in the range of marine carbonates (e.g., Zeebe & Wolf-Gladrow, 2001). The serpentinites with lower TIC content generally have more $^{13}$C-depleted compositions ranging between −8.6‰ and +0.6‰ (Figure 3c).
However, six serpentinites with TIC > 500 ppm, primarily from Hole M0072B, have more 13C-depleted compositions (avg. of −6.3‰) than other serpentinites with high TIC contents. NCC concentrations range from below detection limit to 0.1 wt%, and δ13C varies from −28.3‰ to −19.8‰ (see Figures 5c and 5d). NCC contents are generally below 260 ppm in the mafic rocks and average 309 ppm in the serpentinites, with many higher than 500 ppm. Higher NCC concentrations are observed in the upper meters of the cores and more frequently in deeper sections at Hole M0072B.

4.1.2. Carbonate Veins

The δ13C of the veins lie in a narrow range from −3.0‰ to +2.3‰, typical for marine carbonates (Figure 6 and Table 2). Dolomites have slightly more 13C-depleted compositions of −2.6‰ to +0.2‰ (n = 5). The calcites (n = 16) show a distinction between Holes M0072B and M0076B, with an average δ13C of −1.2‰ and +2.0‰, respectively. δ13C of the aragonite veins range from −1.5‰ to +1.6‰ (n = 7) and show a distinction between Hole M0076B with slightly more depleted compositions (−1.5‰ to −0.1‰) and Hole M0069A (−0.2‰ to +1.6‰).

4.2. Oxygen Isotopes

4.2.1. Bulk Rock Carbonate

The overall inorganic carbon concentration of the mafic rocks is very low; thus, only seven samples could be measured. They have low δ18O values of −15.2‰ to −9.9‰ (VPDB) except for one sample located below a highly brecciated domain with a δ18O of +3.9‰. This is interpreted to be related to late precipitation from seawater (Figure 7a). The ultramafic rocks exhibit a wide range of δ18O values from −19.8‰ to +4.7‰. No downhole trend in δ18O can be observed; however, some general patterns are visible across the different sites. The δ18O from ultramafic rocks from Hole M0071A and Site M0069 show relatively high δ18O ranging between −4.3‰ and +4.7‰ except for one sample with δ18O of −14.4‰. Sites M0072, M0068, and Hole M0071B and M0071C are characterized by overall 18O-depleted compositions between −19.8‰ and −5.3‰. Site M0076, closest to the LCHF, shows δ18O values varying from −13.5‰ to +4.8‰.

4.2.2. Carbonate Veins

The δ18O of the veins vary over a range of −19.1‰ to +4.5‰ (Figures 6 and 7a). Dolomites vary from −16.8‰ to −9.2‰, with one outlier around −14.4‰. The calcite veins from Hole M0072B have the most 18O-depleted compositions from −19.1‰ to −0.7‰ with a decreasing trend with increasing depth (Figure 7a). These 18O-depleted compositions are distinct from the calcite veins in Holes M0076B and M0071A.
| Site | Hole | Core | Section | Interval (cm) | Depth (mbsf) | Lithology               | MBio | TC (ppm) | NCC (ppm) | TIC (ppm) | δ¹³C_TC (‰) | δ¹⁸O_NCC (‰) | δ¹³C_TIC (‰) | δ¹⁸O_TIC (‰) | T° (°C) |
|------|------|------|---------|-------------|-------------|-------------------------|------|----------|-----------|-----------|-------------|---------------|----------------|---------------|------------|---------|
| 71   | A    | 1    | 1       | 45          | 48          | Serpentinitized dunite   | 1,407|          | 384       | 1,000     | −5.92       | −25.88        | 2.18           | 4.38           | 0          |
| 71   | A    | 1    | 2       | 0           | 11          | Serpentinitized dunite   | 39,064|          | 1,108     | 40,630    | 0.71        | −22.03        | 0.30           | 0.36           | 16         |
| 71   | A    | 1    | 2       | 11          | 18          | Serpentinitized dunite   | 49,044|          | 315       | 49,737    | 0.95        | −22.33        | 0.63           | 1.89           | 10         |
| 71   | A    | 1    | 2       | 120         | 121         | Serpentinitized harzburgite | 207  |          |           |           | −20.55      |               |               |               |           |
| 71   | A    | 2    | 1       | 64          | 67          | Metagabbro              | 203  |          |           |           | −26.33      |               |               |               |           |
| 71   | A    | 2    | 1       | 67          | 77          | Metagabbro              | 48   |          | 75        |           | −17.66      | −24.88        |               |               |           |
| 71   | A    | 2    | 1       | 77          | 86          | Metagabbro              | 60   |          | 256       |           | −25.33      | −25.09        |               |               |           |
| 71   | B    | 2    | 1       | 53          | 58          | Serpentinite rubble      | 119  |          | 251       | 63        | −13.57      | −24.63        | −3.64          | −5.32         | 44         |
| 71   | B    | 2    | 1       | 61          | 64          | Serpentinite rubble      | 131  |          | 277       |           | −12.83      | −24.22        |               |               |           |
| 71   | B    | 2    | 1       | 64          | 66          | Serpentinite rubble      | 93   |          | 265       |           | −14.85      | −24.50        |               |               |           |
| 71   | B    | 3    | 1       | 0           | 10          | Serpentinite rubble      | 138  |          | 726       | 136       | −8.18       | −23.10        | −7.96          | −11.15        | 85         |
| 71   | B    | 3    | 1       | 27          | 29          | Serpentinite rubble      | 152  |          | 220       |           | −24.42      | −25.26        |               |               |           |
| 71   | C    | 1    | 1       | 11          | 13          | Serpentinite rubble      | 545  |          | 531°      | 14°       | −24.98      | −7.36         | −9.76          | 74          |
| 71   | C    | 1    | 1       | 46          | 50          | Serpentinitized harzburgite | 262  |          | 318       |           | −22.62      | −25.47        |               |               |           |
| 71   | C    | 2    | 1       | 67          | 77          | Serpentinitized harzburgite | 226  |          | 299       |           | −21.79      | −24.27        |               |               |           |
| 71   | C    | 2    | 1       | 74          | 76          | Serpentinitized harzburgite | 309  |          |           |           | −19.86      |               |               |               |           |
| 71   | C    | 2    | 1       | 78          | 84          | Serpentinitized harzburgite | 130  |          | 225       |           | −11.92      | −23.38        |               |               |           |
| 71   | C    | 2    | 1       | 84          | 90          | Serpentinitized harzburgite | 164  |          | 282       |           | −7.43       | −24.18        |               |               |           |
| 71   | C    | 2    | CC       | 5           | 9           | Serpentinitized harzburgite | 260  |          | 339       |           | −19.93      | −25.42        |               |               |           |
| 71   | C    | 3    | 1       | 0           | 10          | Serpentinitized harzburgite | 180  |          | 268       | 185°      | −8.09       | −25.35        | −8.59          | −14.29        | 114        |
| 71   | C    | 3    | 1       | 10          | 13          | Serpentinitized harzburgite | 151  |          | 322       |           | −20.98      | −23.86        |               |               |           |
| 71   | C    | 5    | 1       | 20          | 23          | Serpentinitized harzburgite | 295  |          | 373       |           | −21.40      | −24.17        |               |               |           |
| 71   | C    | 5    | CC       | 5           | 10          | Serpentinitized harzburgite | 145  |          | 363       |           | −10.68      | −25.41        |               |               |           |
| 71   | C    | 6    | 1       | 55          | 57          | Dolerite rubble          | 801  |          | 679°      | 122°      | −22.82      | −8.15         | −13.08        | 102         |
| 71   | C    | 6    | 1       | 64          | 70          | Dolerite rubble          | 177  |          | 251       |           | −12.45      | −25.93        |               |               |           |
| 71   | C    | 6    | 1       | 70          | 74          | Dolerite rubble          | 213  |          | 252       |           | −10.37      | −25.54        |               |               |           |
| 71   | C    | 6    | 1       | 70          | 74          | Dolerite rubble          | 224  |          | 162       |           | −14.84      | −25.93        |               |               |           |
| 71   | C    | 9    | 1       | 0           | 7           | Serpentinite rubble      | 189  |          | 336       |           | −10.46      | −25.00        |               |               |           |
| 71   | C    | 9    | 1       | 10          | 14          | Serpentinite rubble      | 80   |          | 229       |           | −14.24      | −24.38        |               |               |           |

Table 1: Content and Carbon and Oxygen Isotope Compositions (VDPDB) of Total Carbon (TC), Total Non-Carbonate Carbon (NCC), Total Inorganic Carbon (TIC), and Carbonate Formation Temperature of Gabbroic and Ultramafic Rocks From the Southern Wall at the Atlantis Massif
| Site | Hole | Core | Section | Interval (cm) | Depth (mbsf) | Lithology | MBio | TC (ppm) | NCC (ppm) | TIC (ppm) | δ^13C (‰) | δ^15N (‰) | δ^18O (‰) | θ (°C) |
|------|------|------|---------|--------------|--------------|-----------|------|----------|-----------|-----------|-----------|-----------|------------|-----------|
| 69   | A    | 5    | 1       | 137          | 151          | Serpentinitized harzburgite | 44   | 13.80    | 13.81     | -29.29    | -25.52    | -19.99    | -23.63     | 1.46       |
|      |      |      |         | 11.12        | 11.14        | Serpentinitized harzburgite | 124  | 58.22    | 61.63     | 0.54      | -26.96    | 0.91      | 1.42       | 16.10      |
|      |      |      |         | 16.08        | 16.10        | Serpentinitized harzburgite | 255  | 12,578   | 12,120    | 0.22      | -24.12    | 1.63      | 4.74       | -11.56     |
| 69   | A    | 9    | 2       | 57           | 61           | Serpentinitized harzburgite | 61   | 13.94    | 13.98     | -17.99    | -25.85    | -2.77     | -4.33      | 2         |
|      |      |      |         | 124          | 129          | Serpentinitized dunite | 124  | 5,123    | 4,973     | 0.54      | -26.96    | 0.91      | 1.42       | 11        |
|      |      |      |         | 16.08        | 16.10        | Serpentinitized harzburgite | 255  | 12,578   | 12,080    | 0.22      | -24.12    | 1.63      | 4.74       | -11.56     |
| 69   | A    | 10   | 2       | 80           | 87           | Serpentinitized harzburgite | 87   | 15.52    | 15.59     | -0.71     | -0.44     | 1.52      | 11         | 5          |
|      |      |      |         | 173          | 173          | Serpentinitized harzburgite | 173  | 6,560    | 6,733     | 0.76      | -27.73    | 0.60      | 3.07       | 5         |
| 72   | B    | 5    | 1       | 40           | 43           | Talc/amphi./chlorite schist | 43   | 6.39     | 6.42      | -9.67     | -20.32    | -6.36     | -9.90      | 75        |
|      |      |      |         | 171          | 171          | Talc/amphi./chlorite schist | 171  | 106      | 106       | -22.50    | -25.35    | -24.51    | 1.46       | 3         |
|      |      |      |         | 16.14        | 16.23        | Talc/amphi./chlorite schist | 16.14| 103      | 103       | -4.49     | -16.21    | 3         | 116        | 136       |
| 72   | B    | 7    | 1       | 55           | 55           | Serpentinitized harzburgite | 55   | 9.54     | 9.57      | -11.62    | -4.49     | -16.21    | 3         | 116        |
|      |      |      |         | 16.08        | 16.10        | Serpentinitized harzburgite | 255  | 12,578   | 12,080    | 0.22      | -24.12    | 1.63      | 4.74       | -11.56     |
| 72   | B    | 7    | 1       | 109          | 115          | Talc/amphi./chlorite schist | 115  | 10.08    | 10.14     | -22.70    | -26.58    | -16.07    | 24.07      | 0         |
|      |      |      |         | 115          | 125          | Talc/amphi./chlorite schist | 125  | 10.14    | 10.24     | -24.33    | -26.39    | -24.33    | 0         | 0         |
|      |      |      |         | 126          | 136          | Talc/amphi./chlorite schist | 136  | 10.25    | 10.35     | -26.22    | -25.31    | -26.22    | -25.31     | 0         |
| 72   | B    | 7    | 1       | 126          | 136          | Talc/amphi./chlorite schist | 136  | 10.25    | 10.35     | -23.66    |         |          |            | 0         |
|      |      |      |         | 10.38        | 10.42        | Serpentinitized harzburgite | 10.42| 10.38    | 10.42     | -24.43    | -26.39    | -24.43    | -26.39     | 0         |
|      |      |      |         | 12.00        | 12.02        | Serpentinitized harzburgite | 12.02| 12.18    | 12.20     | -24.43    | -26.39    | -24.43    | 0         | 0         |
| 72   | B    | 8    | 2       | 26           | 30           | Serpentinitized harzburgite | 30   | 11.77    | 11.81     | -17.71    | -6.23     | -18.27    | -19.83     | 191       |
|      |      |      |         | 26.00        | 26.20        | Serpentinitized harzburgite | 26.20| 11.78    | 11.81     | -26.61    | -2.57     | -19.83    | 191       | 1         |
| 72   | B    | 8    | 2       | 50           | 51           | Serpentinitized harzburgite | 51   | 12.00    | 12.02     | -9.05     | -24.88    | -9.05     | -24.88     |          |
|      |      |      |         | 67           | 70           | Serpentinitized harzburgite | 70   | 12.18    | 12.20     | -13.89    | -26.17    | -13.89    | -26.17     | 0         |

Table 1
Continued
Table 1  
Continued

| Site | Hole | Core | Section | Interval (cm) | Depth (mbsf) | Lithology | MBio | TC (ppm) | NCC (ppm) | TIC (ppm) | δ13C_T (‰) | δ18O_T (‰) | δ13C_NCC (‰) | δ18O_NCC (‰) | δ13C_TIC (‰) | δ18O_TIC (‰) | T° (°C) |
|------|------|------|---------|--------------|--------------|-----------|------|----------|-----------|----------|-------------|-------------|--------------|--------------|--------------|-------------|--------------|-------------|
| 72   | B    | 8    | 2       | 76 77       | 12.27 12.28  | Serpentinized harzburgite | 1,372 | 330a 1,042a | −8.00  | −2.47  | −11.48 88 |            |              |              |              |              |              |
| 72   | B    | 8    | CC 0    | 5           | 12.28 12.33  | Serpentinized harzburgite | x    | 759    | 662 650  | −11.91  | −27.98 97 |            |              |              |              |              |              |
| 72   | B    | 8    | CC 5    | 20          | 12.33 12.48  | Serpentinized harzburgite | x    | 532    | 135 1,020 | −5.65  | −27.50 140 |            |              |              |              |              |              |

76 B 3 1 78 83 4.22 4.27 Serpentinized dunite 256 290 −15.16 −25.74
76 B 3 1 100 125 4.44 4.69 Serpentinized dunite x 1,180 303 1,111a 0.72 −19.83 1.99 1.08 13
76 B 3 1 100 125 4.44 4.69 Serpentinized dunite x 655 177 598 0.62 −21.94 1.42 1.03 13
76 B 3 1 102 110 4.46 4.54 Serpentinized dunite x 858 237 802 0.41 −23.52 2.07 3.15 5
76 B 4 2 28 31 6.74 6.77 Serpentinized harzburgite 246 365 31b −24.31 −27.56 −1.60
76 B 5 1 14 28 6.87 7.01 Serpentinized dunite x 398 234 358 7.67 −27.28 −5.49 −13.48 106
76 B 5 1 14 28 6.87 7.01 Serpentinized dunite x 651 279 580 1.86 −25.63 1.04 −1.83 26
76 B 5 1 28 36 7.01 7.09 Serpentinized dunite x 1,384 288 1,080 0.34 −27.98 1.57 −4.41 39
76 B 5 1 55 59 7.28 7.32 Serpentinized dunite 8,092 266 7,808a 1.43 −23.78 2.42 4.26 0
76 B 5 1 77 80 7.50 7.53 Metagabbro 168 144 −18.13 −25.76
76 B 6 1 63 65 8.61 8.63 Serpentinized harzburgite 235 201 −16.90 −25.27
76 B 6 1 118 122 9.16 9.20 Serpentinized harzburgite 356 282 −18.47 −25.55
76 B 7 1 60 62 10.32 10.34 Serpentinized harzburgite 273 221 −19.54 −25.49
76 B 7 1 81 83 10.53 10.55 Serpentinized harzburgite 2,283 146 2,137 0.06 −25.45 1.81 1.73 10
76 B 7 1 95 105 10.67 10.77 Serpentinized harzburgite x 217 235 −10.14 −25.51
76 B 7 1 105 120 10.77 10.92 Serpentinized harzburgite x 234 179 157 12.06 −25.80 −5.34 −10.55 80
76 B 7 1 105 120 10.77 10.92 Serpentinized harzburgite x 509 253 462 2.24 −25.51 0.12 −2.37 29
76 B 8 1 90 94 12.05 12.09 Serpentinized harzburgite 320 288 −21.46 −25.92
76 B 8 1 112 117 12.27 12.32 Serpentinized harzburgite 26,599 10,254a −2.34 −0.24 −6.42 51
76 B 8 1 148 151 12.63 12.66 Serpentinized harzburgite 262 266 −23.46 −26.72
76 B 9 1 34 41 13.21 13.28 Serpentinized harzburgite x 10,414 164 10,860 0.60 −28.31 0.31 4.75 1
76 B 9 1 43 52 13.30 13.39 Serpentinized harzburgite x 101 151 49a −16.67 −25.25 −7.72 −6.73 53
76 B 10 1 91 111 15.50 15.70 Serpentinized dunite x 136 120 45 21.31 −27.90 −7.90 −7.93 61
76 B 10 1 91 111 15.50 15.70 Serpentinized dunite x 1,567 147 1,540 1.14 −28.00 1.68 0.86 14

68 A 1 1 12 21 0.12 0.21 Talc/amphi. schist x 63 213 −13.36 −24.29
68 B 1 1 10 13 0.10 0.13 Serpentinized harzburgite 85 158 −24.69 −25.57
68 B 1 1 34 35 0.34 0.35 Serpentinized harzburgite 219 −25.27
68 B 1 1 38 40 0.38 0.40 Serpentinized harzburgite 531 48 48 23.88 8.21 −13.85 110
68 B 1 1 132 135 1.32 1.35 Metagabbro 72 161 3 15.41 −25.07 −6.92 −11.77 90
4.3. Carbonate Precipitation Temperatures

4.3.1. Bulk Rock Oxygen Isotope Temperatures

Figure 7b shows estimated temperatures calculated from the bulk rock oxygen isotope data, using the equation O’Neil et al. (1969) corrected in Friedman & O’Neil (1977), assuming that all carbonate is calcite and using a δ¹⁸O fluid of 0.4‰ (VSMOW), the end-member LCHF vent fluid composition (Kelley et al., 2005). The calculated carbonate formation temperatures range from ambient to 191°C, with the highest temperatures observed in Hole M0072B. Carbonates from the mafic rocks formed exclusively at higher temperatures between 75°C and 124°C, with one exception giving ambient temperatures. The ultramafic rocks exhibit a wide range of temperatures but show no downhole trends; however, some general patterns are apparent across the different sites. Carbonates from Hole M0071A and Site M0069 formed at temperatures <39°C, except for the deepest serpentinite of Hole M0069A that has a temperature of >100°C. Carbonates from Sites M0072 and M0068 and Holes M0071B and M0071C are characterized by precipitation temperatures of 44°C–191°C, with Site M0072 showing the highest temperatures consistently >88°C. Site M0076 shows a wide range of temperatures varying from ambient to 106°C.

Two samples from different sites and depths have calculated precipitation temperatures slightly below 0°C, inconsistent with minimum seawater temperatures in the area. However, negative temperatures have been reported previously in peridotite-hosted carbonate veins (e.g., Bonatti et al., 1980; Eickmann et al., 2009; Früh-Green et al., 2003). Atmospheric CO₂ is enriched by ~1.2‰ higher than present-day (Schrag et al., 2002). Another possibility is that rock-dominated fluid-rock interaction produced fluids with higher δ¹⁸O values than assumed. For example, calculated temperatures would be higher by 5°C–10°C if a δ¹⁸O fluid of +2‰ is used.

4.3.2. Clumped Isotope Temperatures of Carbonate Veins

Clumped isotope temperatures of the serpentinite-hosted carbonate veins vary from ambient to 196°C, a range similar to that calculated from the δ¹⁸O of whole-rock samples of the serpentinites (Table 2). The calcite veins show the highest variability of formation temperatures, from ambient to 184°C, whereas dolomite veins have formation temperatures between 70°C and 196°C, except for one outlier at 33°C. The consistency of the clumped isotope temperatures with those estimated from δ¹⁸O suggests that the maximum temperatures of precipitations are preserved, and the carbonates have not undergone bond reordering upon cooling. Within this range, clear groups can be identified. The calcite veins from Hole M0072B show the highest temperatures with a distinction between moderate temperatures (T₄₇ = 40°C) in the upper section and high temperatures (T₄₇ = 152°C) below 11 mbsf (Figure 7b). The higher temperatures distinctly separate calcite veins in Hole M0072B from the calcite veins in Holes M0076B and M0071A, which formed at low temperatures with T₄₇ < 22°C. Aragonite veins show temperatures of less than 7°C, similar to calcite veins from Hole M0076B and M0071A. One calcite vein shows Δ₄₇—temperatures slightly below 0°C, indicating disequilibrium precipitation. Possible mechanisms causing high Δ₄₇ are discussed in detail in Section 4.3.1.

Calculated oxygen isotope values of the fluid in equilibrium with the carbonates vary from ~1.1‰ to +5.4‰. Circulating fluids in equilibrium with dolomite veins yield a range from ~1.1‰ to +2.3‰. Calcite veins yield the most variable oxygen isotope values from −0.5‰ to +5.4‰, with a clear distinction between different sites. The fluids from Site M0072 have an average δ¹⁸O of +0.1‰, whereas Site M0076 (avg. of +2.2‰) and M0071 (δ¹⁸O = +3.4‰) have more δ¹⁸O-enriched compositions. The aragonite veins show a restricted range of oxygen isotopic compositions similar to dolomite with δ¹⁸O fluid = −0.1‰ to +1.6‰.
Figure 4. (a) Variations in total carbon (TC) content. (b) $\delta^{13}$C_{TC} values with depth below seafloor (mbsf) in serpentinized peridotites, gabbroic rocks, and metasomatic fault rocks from the southern wall at the AM. Average isotopic composition of mantle and seawater carbon are shown as dashed lines. Grey shaded region marks the range of TC content at the southern wall from the previous study of Delacour, Früh-Green, Bernasconi, Schaeffer, and Kelley (2008).

Figure 5. (a) Variations in total inorganic carbon (TIC). (b) $\delta^{13}$C_{TIC}. (c) Total non-carbonate carbon (NCC). (d) $\delta^{13}$C_{NCC} with depth below seafloor in serpentinized peridotites, gabbroic rocks, and metasomatic fault rocks at the southern wall at the Atlantis Massif. Average isotopic composition of mantle and seawater carbon are shown as dashed lines. Grey shaded region marks the range of TIC, NCC, and isotopic composition at the southern wall from the previous study of Delacour, Früh-Green, Bernasconi, Schaeffer, and Kelley (2008).
4.4. Carbonate Types

The carbon and oxygen isotope composition of the carbonates allows distinguishing two groups of samples (Figure 6). Type I is characterized by $^{13}$C- and $^{18}$O-depleted compositions and corresponds to the whole-rock samples with low TIC concentrations. The calculated formation temperatures range from 49 to 191°C. Type II is characterized by higher TIC contents, with $^{13}$C-enriched compositions and precipitation temperatures $<$40°C. Some samples plot between the two groups suggesting a mixture of Type I and Type II.

4.5. Radiocarbon Dating

Radiocarbon ages were determined on four whole-rock samples, four dolomite, seven calcite, and three aragonite veins, and five decarbonated whole-rock samples (representing NCC) from four sites (Table 3) and yielded values from 38,393 to 1,518 yr. Carbonate veins have $^{14}$C ages ranging from 37,438 to 23,355 yr. The dated veins often contain multiple generations of carbonate, which could not be physically separated; therefore, the $^{14}$C ages can represent a mixture of different generations. The dolomites gave the oldest ages from 37,438 to 27,745 yr, and a distinct increase in age with depth is observed at Hole M0076 (Figure 7b). Calcite $^{14}$C ages range from 34,647 to 23,355 yr, which are slightly younger than the dolomites and show no distinct pattern across the sites (Figure 8 and Table 3). Aragonite veins range from 34,057 to 24,556 yr, with a clear distinction between old aragonite at Hole M0069A and younger aragonite at Hole M0076B (avg. $\sim$26 Kyr).

Total bulk carbon has a range of $^{14}$C values between 32,854 and 5,754 yr, which are, in part, younger ages than the veins (Table 3). While samples from Hole M0069A and M0076B exhibit bulk rock ages in the range of the nearby veins ($\sim$31 Kyr), distinctly younger ages ($\sim$6 Kyr) are measured in Hole M0072B. The radiocarbon ages of the bulk NCC (decarbonated samples) from all three central sites are much younger and more uniform (Figure 8 and Table 3). $^{14}$C NCC ages range from 16,103 to 8,355 yr, whereby the youngest age was measured at Hole M0076B. The $^{14}$C of the inorganic carbon was calculated by mass balance using radiocarbon ages and content of TC and total NCC. The $^{14}$C ages of TIC range from 38,393 to 1,518 yr, and the estimated ages from Hole M0069A and M0076B coincide with $^{14}$C ages from carbonate veins from the same hole. However, TIC from Hole M0072B has the youngest ages (avg. 3,363 yr) and is distinctly different from the carbonate veins in that hole.
## Table 2

*Clumped Isotope Composition of Carbonate Veins and Calculated δ¹⁸O of the Fluid in Ultramafic Rocks From the Southern Wall at the Atlantis Massif*

| Site | Hole | Core | Section | Top | Bot. | Top | Bot. | Lithology | Mineral | n   | δ¹⁸O<sub>vein</sub>(VPDB) (%) | σ   | δ¹⁴C<sub>vein</sub>(VPDB) (%) | σ   | Δ47 (%) | σ   | Temperature (°C) | δ¹⁸O<sub>fluid</sub>(SMOW) (%) | 68% |
|------|------|------|---------|-----|------|-----|------|-----------|---------|-----|------------------------|------|---------------------|------|----------|------|-----------------|-------------------|-----|
| 71   | A    | 1    | 1       | 24  | 28   | 0.24| 0.28| Serpentined dunite | Calcite | 11  | 2.26                    | 0.09 | 3.90                | 0.19 | 0.690              | 0.073 | 22               | 7                 | 5.35 |
| 69   | A    | 9    | 2       | 57  | 61   | 13.94| 13.98| Serpentined harzburgite | Aragonite | 6   | −0.22                   | 0.02 | 4.22                | 0.04 | 0.750              | 0.010 | 4                 | 1                 | 1.40 |
| 69   | A    | 10   | 1       | 15  | 18   | 14.87| 14.90| Serpentined harzburgite | Aragonite | 9   | 1.56                    | 0.03 | 3.51                | 0.05 | 0.742              | 0.032 | 7                 | 3                 | 1.17 |
| 69   | A    | 10   | 1       | 104 | 124  | 15.76| 15.96| Serpentined harzburgite | Aragonite | 7   | 1.16                    | 0.02 | 3.83                | 0.02 | 0.740              | 0.016 | 7                 | 2                 | 1.55 |
| 72   | B    | 7    | 1       | 28  | 30   | 9.27| 9.29 | Serpentined dunite | Calcite | 3   | 0.18                    | 0.00 | −0.71               | 0.52 | 0.613              | 0.045 | 45                | 12                | -     |
| 72   | B    | 7    | 1       | 28  | 30   | 9.27| 9.29 | Serpentined dunite | Calcite | 2   | −0.07                   | 0.05 | −4.36               | 0.50 | 0.637              | 0.032 | 36                | 4                 | −0.02 |
| 72   | B    | 7    | 1       | 28  | 30   | 9.27| 9.29 | Serpentined dunite | Calcite | 8   | −0.65                   | 0.12 | −11.11              | 0.86 | 0.569              | 0.022 | 62                | 12                | -     |
| 72   | B    | 7    | 1       | 75  | 77   | 9.74| 9.76 | Serpentined harzburgite | Calcite | 10  | 0.22                    | 0.05 | −1.44               | 0.13 | 0.605              | 0.032 | 33                | 4                 | −0.54 |
| 72   | B    | 7    | 1       | 75  | 77   | 9.74| 9.76 | Serpentined harzburgite | Calcite | 3   | −2.09                   | 0.04 | −7.05               | 0.05 | 0.643              | 0.011 | 34                | 3                 | -     |
| 72   | B    | 8    | 1       | 19  | 22   | 10.90| 10.93| Serpentined harzburgite | Calcite | 5   | −0.26                   | 0.08 | −2.77               | 0.38 | 0.658              | 0.025 | 30                | 4                 | 0.23 |
| 72   | B    | 8    | 1       | 19  | 22   | 10.90| 10.93| Serpentined harzburgite | Calcite | 10  | −3.03                   | 0.15 | −17.90              | 0.37 | 0.430              | 0.055 | 146               | 14                | −0.51 |
| 72   | B    | 8    | 1       | 69  | 72   | 11.40| 11.43| Serp. harz. and talc./amphi. schist | Calcite | 1   | −1.06                   | -    | −16.91              | -    | 0.425              | -      | 144               | -                 | -     |
| 72   | B    | 8    | 1       | 69  | 72   | 11.40| 11.43| Serp. harz. and talc./amphi. schist | Calcite | 8   | −0.69                   | 0.04 | −16.92              | 0.05 | 0.427              | 0.030 | 144               | 9                 | 0.34 |
| 72   | B    | 8    | 2       | 26  | 30   | 11.77| 11.81| Serpentined harzburgite | Calcite | 8   | −2.72                   | 0.04 | −19.12              | 0.20 | 0.383              | 0.019 | 184               | 8                 | 0.74 |
| 72   | B    | 8    | 2       | 67  | 70   | 12.18| 12.20| Serpentined harzburgite | Calcite | 1   | −1.74                   | -    | −18.67              | -    | 0.424              | -      | 145               | -                 | -     |
| 72   | B    | 8    | 2       | 67  | 70   | 12.18| 12.20| Serpentined harzburgite | Calcite | 2   | −2.23                   | 0.02 | −17.84              | 0.09 | 0.421              | 0.024 | 149               | 25                | -     |
| 76   | B    | 5    | 1       | 48  | 50   | 7.21| 7.23 | Serpentined dunite | Dolomite | 8   | −1.87                   | 0.01 | −16.77              | 0.07 | 0.343              | 0.012 | 196               | 6                 | 2.32 |
| 76   | B    | 5    | 1       | 48  | 50   | 7.21| 7.23 | Serpentined dunite | Dolomite | 10  | 2.15                    | 0.03 | 3.59               | 0.08 | 0.730              | 0.027 | 9                 | 2                 | 2.11 |
| 76   | B    | 5    | 1       | 55  | 59   | 7.28| 7.32 | Serpentined dunite | Dolomite | 4   | 1.72                    | 0.23 | 3.82               | 0.52 | 0.783              | 0.023 | −3                | 3                 | -     |
| 76   | B    | 5    | 1       | 55  | 59   | 7.28| 7.32 | Serpentined dunite | Dolomite | 12  | 2.21                    | 0.01 | 4.45               | 0.03 | 0.740              | 0.022 | 7                 | 2                 | 2.32 |
| 76   | B    | 8    | 1       | 112 | 117  | 12.27| 12.32| Serpentined harzburgite | Dolomite | 9   | −1.21                   | 0.03 | −14.56              | 0.13 | 0.386              | 0.035 | 154               | 11                | 1.78 |
| 76   | B    | 8    | 1       | 112 | 117  | 12.27| 12.32| Serpentined harzburgite | Dolomite | 1   | −0.86                   | -    | −13.04              | -    | 0.511              | -      | 70                | -                 | -     |
| 76   | B    | 9    | 1       | 5   | 9    | 12.92| 12.96| Serpentined harzburgite | Aragonite | 7   | −0.12                   | 0.02 | 3.87               | 0.04 | 0.770              | 0.009 | 0                 | 1                 | −0.09 |
| 76   | B    | 9    | 1       | 5   | 9    | 12.92| 12.96| Serpentined harzburgite | Aragonite | 9   | −0.69                   | 0.02 | 4.43               | 0.07 | 0.770              | 0.033 | 0                 | 3                 | 0.57 |
| 76   | B    | 9    | 1       | 5   | 9    | 12.92| 12.96| Serpentined harzburgite | Dolomite | 12  | −2.64                   | 0.03 | −9.20               | 0.10 | 0.503              | 0.034 | 75                | 5                 | −1.09 |
### 5. Discussion

Our data suggest at least three forms of carbonate precipitation in the basement rocks of the AM: (a) dispersed carbonization; (b) hydrothermal carbonate vein formation; and (c) aragonite and calcite precipitation in veins at ambient temperatures. These carbonates allow critical new insights into fluid flow and mass transfer within a serpentinite–hosted hydrothermal system. In the following, we discuss the evolution of carbonate formation in the AM and then discuss the implications for organic carbon storage in the oceanic crust.

#### 5.1. Continuous Dispersed Carbonate Precipitation

Early stages of alteration of the AM are characterized by pervasive serpentinization, which leads to the formation of serpentine mesh textures after olivine at temperatures between 200°C and 350°C, as is commonly observed in diverse geodynamic contexts (Rouméjon, Früh-Green, et al., 2018). The water is supplied via a fine network along grain boundaries, which leads to the formation of the earliest Type I carbonates with progressive hydration and cooling of the basement at temperatures from 190°C to 50°C (Figure 9a). These temperatures are calculated from bulk rock $^{18}$O$_{H_{2}O}$ compositions and may represent a mixture of even higher ($T < 250^\circ$C, Frost & Beard, 2007) and lower formation temperatures. Dispersed carbonates are found throughout the southern wall. Radiocarbon ages indicate precipitation has continued from over 38 Kyr ago to 1.5 Kyr locally at the central sites. This suggests that dispersed carbonate formation is associated with progressive hydrothermal circulation and serpentinization of the AM and is likely still active at shallow crustal levels today (Figure 8). This hypothesis is consistent with the results of Proskurowski et al. (2008), who showed that DIC concentrations in the Lost City vent fluids are extremely low and suggested that serpentinization and carbonization are ongoing processes.

Type I carbonates have a distinct isotopic signature indicating a $^{13}$C-depleted DIC source (Figure 6). Highly depleted $^{13}$C compositions are typical for organic carbon; and in submarine low-temperature hydrothermal systems, two sources for $^{13}$C-depleted DIC are possible: (a) biologically mediated respiration of organic matter (OM) and (b) abiotic hydrothermal degradation of DOM from seawater-derived fluids. A third less depleted but relatively light carbon source is magmatic volatiles ($\text{CH}_4$, $\text{CO}_2$) trapped in plutonic and mantle rocks. $\text{CO}_2$ and HCO$_3^-$ can be actively produced from organisms living within the ultramafic and mafic rocks or can be produced by biologically mediated respiration of OM, transported via the circulating fluid, and stored in the basement rocks. Recent microbiological and metagenomic studies indicate that microbial life can be sustained within the lithosphere and provide evidence that microbial utilization of $\text{H}_2$, $\text{CH}_4$, and formate may be common in different serpentinization systems (e.g., Brazelton et al., 2012; Lang et al., 2018; Schrenk et al., 2013). Furthermore, micron-scale OM has been detected encapsulated in serpentinized peridotites at sites along the MAR (Ménez et al., 2012, 2018). Motamedi et al. (2020) were able to identify Thermoplasmata, Acidobacteria, Acidimicrobia, and Chloroflexi as organisms potentially living within the ultramafic rocks at the AM. However, the currently known temperature limit for life is 122°C (Takai et al., 2008), and our results show that Type I carbonates precipitated at temperatures up to 191°C, well above this limit. Therefore, we propose that biologically mediated respiration of OM within the basement is unlikely as a carbon source for Type I carbonates or only contributes a minor amount of $^{13}$C-depleted carbon.

Another possible source for $^{13}$C-depleted DIC is the abiotic hydrothermal decay of DOM transported into the rocks by circulating seawater. Part of marine DOM is known to be very stable in deep ocean water and is mostly unaffected by consumption, oxidation, and reactive surface processes over long periods of time, as indicated by an average DOM age of 4,000 to 6,400 $^{14}$C yr (Druffel & Griffin, 2015; Flerus et al., 2012). One possible way to remove the oldest and most recalcitrant forms of DOM from seawater is thermal degradation during hydrothermal alteration of the oceanic crust (Hawkes et al., 2015; Lang et al., 2006; McCollom & Seewald, 2003; Seewald, 2001). The presence of organic compounds such as isoprenoids (pristane, phytane, and squalene), polycyclic compounds (hopanes and steranes), and higher abundances of $\text{n-C}_{16}$ to $\text{n-C}_{26}$ alkanes at the
central dome of the AM down to 1,095 mbsf (IODP Site U1309) implies seawater circulation and transport of DOM deep into the basement (Delacour, Früh-Green, Bernasconi, Schaeffer, & Kelley, 2008). In these environments, abiotic oxidation of DOM by water, nitrate, sulfate, and oxidized minerals (Bischoff & Seyfried, 1978; McCollom & Seewald, 2003; Seewald, 2001; Zhang et al., 2007) followed by decarboxylation (McCollom & Seewald, 2003; Seewald, 2001) can lead to a stepwise decrease in molecular weight of DOM, production of $^{13}$C-depleted CO$_2$ and CH$_4$ and, ultimately, the removal of DOM from solution (McCollom & Seewald, 2003). Hawkes et al. (2015, 2016) and Rossel et al. (2017) recently performed hydrothermal experiments with marine DOM using fluid samples from nine different vent fields from the Atlantic, Pacific, and the Southern Oceans to study abiotic degradation of solid-phase extractable DOM in a temperature range from 100°C to 380°C. These studies indicate that the vast majority of solid-phase extractable DOM cannot survive hydrothermal circulation at temperatures >380°C. At temperatures between 100°C and 200°C, only some low-molecular-weight, oxygen-depleted, and heteroatom (N, S, P) species may survive. Extrapolation of their data suggests that substantial alteration of DOM may start at 68°C ± 14°C (Hawkes et al., 2015, 2016). Our results indicate a minimum temperature of 50°C–190°C, which is sufficiently elevated for the efficient degradation of solid-phase extractable-DOM. Thus, we argue that the abiotic hydrothermal decay of DOM very likely occurs during circulation of the hydrothermal fluid within the AM basement and that this carbon source is the main input for Type I carbonate formation.

A subset of Type I carbonates is characterized by $\delta^{13}$C between −5.0‰ and −2.1‰. For this range of compositions, lighter mantle CO, CO$_2$, or CO$_2$ derived from the oxidation of CH$_4$ and other short-chain hydrocarbons released from fluid inclusions is an additional possible DIC source. Mantle carbon has a bimodal range with $\delta^{13}$C clustering around −5‰ and −25‰ (Deines, 2002). Thus, $^{13}$C-depleted carbon derived from volatiles leached from the mafic and ultramafic basement sequences is potentially an additional carbon source for Type I carbonates. Methane observed in fluid inclusions in the Southwest Indian Ridge plutonic rocks is characterized by $\delta^{13}$C of −10‰ to −30‰ (Kelley et al., 2002; Kelley & Früh-Green, 1999, 2001), a range that matches the composition of methane measured at the Lost City vents (−16‰ to −9‰; Proskurowski et al., 2008), as well as other hydrothermal systems such as the Von Damm field at the Cayman Rise.
Table 3
Radiocarbon Ages of Carbonate Veins in Ultramafic Rocks and Whole-Rock Samples From the Southern Wall at the Atlantis Massif

| Site | Hole | Core | Section | Interval (cm) | Depth (mbsf) | Lithology | Mineral | Sample type | Carbon type | F^14C | 14C ages (yr) | σ |
|------|------|------|---------|-------------|-------------|-----------|---------|-------------|-------------|-------|----------------|---|
| 71   | A    | 1    | 2       | 0           | 5           | 0.58      | 0.63    | Serpentized dunite | Calcite | vein | inorganic | 0.019 | 3.39 | 31,902 | 339 |
| 69   | A    | 9    | 2       | 57          | 61          | 13.94     | 13.98   | Serpentized harzburgite | Aragonite | vein | inorganic | 0.014 | 3.66 | 34,057 | 410 |
| 69   | A    | 9    | 2       | 106         | 114         | 14.43     | 14.51   | Serpentized dunite | —        | whole rock | non-carbonate | 0.157 | 1.49 | 14,886 | 116 |
| 69   | A    | 9    | 2       | 106         | 114         | 14.43     | 14.51   | Serpentized dunite | —        | whole rock | inorganic | 0.008 | 0.032 | 38,393 | 6 |
| 72   | B    | 7    | 1       | 28          | 30          | 9.27      | 9.29    | Serpentized dunite | Calcite | vein | inorganic | 0.045 | 2.88 | 24,928 | 246 |
| 72   | B    | 7    | 1       | 75          | 77          | 9.74      | 9.76    | Serpentized harzburgite | Calcite | vein | inorganic | 0.013 | 4.76 | 34,647 | 595 |
| 72   | B    | 7    | 1       | 75          | 77          | 9.74      | 9.76    | Serpentized harzburgite | Dolomite | vein | inorganic | 0.029 | 2.89 | 28,438 | 287 |
| 72   | B    | 8    | 1       | 19          | 22          | 10.90     | 10.93   | Serpentized harzburgite | Calcite | vein | inorganic | 0.040 | 3.09 | 25,778 | 252 |
| 72   | B    | 8    | 2       | 26          | 30          | 11.77     | 11.81   | Serpentized harzburgite | —        | whole rock | non-carbonate | 0.135 | 1.04 | 16,103 | 119 |
| 72   | B    | 8    | 2       | 26          | 30          | 11.77     | 11.81   | Serpentized harzburgite | Calcite | vein | inorganic | 0.055 | 2.61 | 23,355 | 224 |
| 72   | B    | 8    | CC      | 0           | 5           | 12.28     | 12.33   | Serpentized harzburgite | —        | whole rock | total | 0.489 | 1.00 | 5,754 | 76 |
| 72   | B    | 8    | CC      | 0           | 5           | 12.28     | 12.33   | Serpentized harzburgite | —        | whole rock | non-carbonate | 0.155 | 1.45 | 14,956 | 118 |
| 72   | B    | 8    | CC      | 0           | 5           | 12.28     | 12.33   | Serpentized harzburgite | —        | whole rock | inorganic | 0.828 | 1,518 | 1.518 |
| 72   | B    | 8    | CC      | 5           | 20          | 12.33     | 12.48   | Serpentized harzburgite | —        | whole rock | total | 0.478 | 0.70 | 5,933 | 71 |
| 72   | B    | 8    | CC      | 5           | 20          | 12.33     | 12.48   | Serpentized harzburgite | —        | whole rock | non-carbonate | 0.136 | 1.65 | 16,050 | 133 |
| 72   | B    | 8    | CC      | 5           | 20          | 12.33     | 12.48   | Serpentized harzburgite | —        | whole rock | inorganic | 0.523 | 5.208 | 5.208 |

*Calculated ages using mass balance, whole-rock ages, and carbon content of non-carbonate and inorganic components.

(CH_4 = −15.4‰; McDermott et al., 2015) where magmatic volatile-rich fluid inclusions are suggested to be a source of methane. In addition, CH_4 at the LCHF is radiocarbon free (Proskurowski et al., 2008), which is consistent with an interpretation that CH_4 and other reduced carbon phases may be derived from volatile-rich fluid inclusions in the AM basement (Labidi et al., 2020).

Carbonates occur in the cores of fully serpentinized olivines. The sizes of these carbonates are, in general, < 20 μm, which is too small for in situ isotope investigations. Thus, we can only assume that the carbonates in the olivine cores are part of the dispersed carbonates and contribute to the depleted whole-rock 13C compositions. Assuming that the abiogenic alteration of OM is the main source of 13C-depleted carbon and that OM is preferentially stored within the serpentine mesh cores replacing olivine, it is possible that in situ oxidation of OM creates low molecular weight organic acids. In the end, organic acids can decay with mineral cataly-
sis to form $^{13}$C-depleted CO$_2$ and CH$_4$ within the serpentine mesh cores. These compounds could be further oxidized and react with Ca$^{2+}$ and Mg$^{2+}$ to form carbonates. A higher concentration of organic compounds inside cores of serpentinite mesh textures has been previously reported by Pliquimper et al. (2017) and Ménez et al. (2018) from the South Chamorro Mud Volcano (Izu-Bonin-Mariana subduction zone) and the central dome of the AM, respectively. Thus, it is likely that carbonates precipitating in various hydrothermal systems can preserve clear isotopic signatures of OM decay for long periods of time and may be an important aspect to fully understand the fate of organic carbon in hydrothermal systems.

5.2. Carbonate Precipitation During Progressive Focused Fluid Flow

As the footwall reaches shallow crustal levels, fluid flow is dominated by continuous fracture planes and microfracturing caused by serpentinization. This forms permeability pathways and channels the fluids along specific domains of the mesh-textured serpentinites (Rouméjon, Früh-Green, et al., 2018). Recrystallization of the mesh texture to chrysotile-dominated and banded veins (Rouméjon, Früh-Green, et al., 2018) indicates a transition from pervasive to localized serpentinization. Our studies indicate that focused fluid flow leads to the formation of carbonate veins in the central part of the AM at temperatures between 30°C and 196°C, depending on the location (Figure 9b).

High-temperature dolomite veins ($T_{\Delta 47} = 70°C–196°C$) are found in the borehole closest to the LCHF, whereas the other central site shows a distinction between shallow ($T_{\Delta 47} = 40°C$) and deeper calcites ($T_{\Delta 47} = 152°C$), indicating locally distinct and variable fluid circulation. A change from pervasive to localized and focused fluid flow at the central sites is consistent with previous work from Boschi et al. (2006), Karson et al. (2006), and Kelley et al. (2005), who proposed that the currently active venting at Lost City is controlled by steeply dipping normal faults. These normal faults allow deeper fluid circulation and serpentinization beneath that area of the massif and channel flow upward through the LCHF. The carbonate veins $^{87}$C from $-3.0‰$ to $+0.2‰$ are less $^{13}$C-depleted than Type I carbonates (Figure 6), which suggests a dominance of DIC derived from seawater with minor contributions of $^{13}$C-depleted carbonate from magmatic volatiles and/or degradation of DOC. Alternatively, the more $^{13}$C-depleted carbonate veins could also be explained by Rayleigh distillation of DIC in the fluid caused by progressive precipitation of carbonate. Assuming precipitation from seawater DIC ($^{13}$C = 0‰) and a fractionation factor between DIC and calcite of 2‰ (i.e., with the calcite being 2‰ heavier than the DIC), removal of about 90% of the original seawater results in a residual DIC in solution with a $^{13}$C of $\sim$5‰. This residual DIC would result in precipitation of carbonates with $^{13}$C of $\sim$3‰, which is within the range observed in the carbonate veins.

The radiocarbon ages from 37 to 23 Kyr (Figure 8) confirms previously reported $^{14}$C ages for the LCHF carbonate towers and veins from Früh-Green et al. (2003), who showed that hydrothermal activity started at least 30 Kyr ago. If we consider that Ludwig et al. (2011) reported much older U/Th ages of the oldest LCHF chimneys of 120 Kyr, it is possible that the $^{14}$C ages could also represent a mixture of carbonates precipitated >37 Kyr ago and younger (or modern) carbonate. This is consistent with results from Proskurowski et al. (2008), who showed that the LCHF vent fluids have very low inorganic carbon contents and argued that ongoing carbonate precipitation within the basement leads to DIC removal. It is likely that carbonate precipitation associated with extensive focused fluid flow has occurred over a longer period of time than that indicated by the radiocarbon ages and is likely an ongoing process in deeper areas below the LCHF.

5.3. Late-Stage, Fracture-Controlled Carbonate Formation

As the AM was progressively unroofed and uplifted, late-stage normal faults formed and created new hydration pathways along brittle fault planes. Underwater camera imagery shows that brittle deformation is widespread along the southern wall of the AM, indicating that a series of faults, rather than a single detachment, accommodated the uplift displacement (Blackman et al., 2002; Karson et al., 2006). Microstructural analysis shows that brittle deformation is concentrated in a section within 50–100 m below the sedimentary cover of the massif (Karson et al., 2006). It is possible that continued circulation of fluids as the massif was uplifted and cooled has led to calcite and aragonite veins at temperatures <40°C and Type II carbonates in the bulk rock (Figure 9c). Thus, we propose that Type II carbonates mainly reflect low-temperature aragonite and
calcite veins. This late-stage carbonate formation increases near the summit of the massif and occurred throughout the southern wall and possibly throughout the entire AM.

Type II carbonates and the carbonate veins that form during this late stage have carbon isotope signatures that suggest that DIC from seawater is the dominant carbon source and that the fluid represents fairly unmodified seawater that only interacted with the basement to a low degree (Figure 6). Calculated $\delta^{18}O$ of the fluids in equilibrium with the vein carbonates are $\sim+1.5\%_\circ \pm 2\%_\circ$, which is identical to seawater and provides additional evidence that seawater bicarbonate is the main carbon source. Late-stage aragonite precipitation at ambient temperatures is a common feature of shallower parts of submarine hydrothermal systems and has been previously described by Alt and Shanks (1998) and Blusztajn and Hart (1996).

Figure 8. Schematic representation of time-line of carbonate formation based on radiocarbon ages of carbonate veins, total inorganic-, and non-carbonate carbon from the three central Sites M0069A, M0072B, and M0076B. Carbonate formation temperatures are based on clumped isotope measurements.

Figure 9. Schematic sketch illustrating the sequence of hydration and carbonation processes affecting mantle rocks at the Atlantis Massif. See text for detailed discussion.
Summarizing, the formation of dispersed carbonates most likely represented the first carbonization phase and occurred at temperatures of 50°C–190°C, with a $^{13}$C-depleted carbon source probably derived from the abiotic hydrothermal decomposition of dissolved organic matter (DOM). Dispersed precipitation of carbonate in the basement progressed with continuous hydration of the AM until at least 1,500 years ago. This is followed by dolomite, magnesite, and calcite precipitation in veins, associated with focused fluid flow at temperatures between 30°C and 196°C, and seawater DIC as the dominant carbon source. These carbonates exhibit $^{14}$C ages from approximately 37–23 Kyr and are characterized by variable carbon isotope signatures following a Rayleigh distillation trend. Late-stage precipitation of aragonite and calcite in veins under ambient temperatures was likely driven by seawater circulation during uplift and progressive brittle fracturing of the massif.

5.4. Serpentinites as a Potential Sink for Marine DOC?

Recent studies have provided evidence that the ultramafic basement can sustain microbial life (Barry et al., 2019; Colman et al., 2017; Fullerton et al., 2019), and the carbon isotope composition of carbonates from this study show that $^{13}$C-depleted, potentially organic carbon, is a significant carbon source in the system. In general, organic carbon concentrations in oceanic serpentinites are highly variable. Compilation of data from Hess Deep, MARK, SWIR, Caiman Rise, Iberian Margin, Vema FZ, AM, Mariana, and the Tyrrhenian Sea of Früh-Green et al. (2004, reference therein) showed that TOC ranges from 30 to 2,700 ppm in oceanic ultramafic and 20–1,000 ppm in mafic rocks. The highest NCC contents measured in our study are $\sim$800 ppm in the ultramafic rocks, $\sim$500 ppm in talc-amphibole-chlorite schists, and $\sim$250 ppm in the gabbroic rocks. No clear distinctions in concentrations of NCC are observed between the mafic and ultramafic rocks (Figure 5c), which suggests that the pervasive fluid flow associated with dispersed carbonate precipitation throughout the AM is likely the main mechanism of DOC transport. Thus, we hypothesize that abiotic hydrothermal decay of DOM and pervasive fluid flow leads to the $^{13}$C-depleted carbon of Type I carbonates, and more focused fluid flux only has a minor influence on NCC content.

The isotopic composition of NCC in the serpentinites from the AM ($\delta^{13}$C$_{NCC} = -28.3\%$ to $-19.8\%$) coincides only in part with the average $\delta^{13}$C of DOC of the North Atlantic, which ranges from $-23.1\%$ to $-22.2\%$ (Eadie et al., 1978; Jeffrey, 1969). The samples with lower $\delta^{13}$C can be affected by preferential removal of compounds enriched in $^{13}$C or could have a contribution from another more $^{13}$C-depleted source of carbon. Delacour, Früh-Green, Bernasconi, Schaeffer, and Kelley (2008) suggested a mixture of dissolved or particulate organic carbon from seawater circulation combined with minor in situ production through the microbial activity as the TOC source in the gabbroic rocks from the central dome of the AM. Motamedi et al. (2020) were able to determine microbial groups that may live within the basement of the AM and lead to in situ production of organic carbon. However, in our study, serpentinized peridotites and talc-amphibole-chlorite schists with the highest NCC content are located at the central Site M0072 below $\sim$11 mbsf. This section is characterized by high calcite formation temperatures ($T_{calcite} = 184^\circ$C) above the currently known temperature limit for life of 122°C (Takai et al., 2008). This observation makes in situ production of organic carbon compounds at Site M0072 during carbonate formation unlikely but does not exclude its formation at other locations and later transport to the central sites or in situ production after carbonate formation.

The average radiocarbon age of NCC in the serpentinized peridotites is 14 Kyr, which is, for the most part, younger than the inorganic carbon in veins and whole rocks. This suggests that older DOM is largely removed or decomposed and may be incorporated in Type I carbonates, and only younger and more recently transported DOM is present as NCC in the rocks. One exception is the dispersed Type I carbonates from the central Site M0072 that have an average age of $\sim$3 Kyr, which is younger than the NCC at the same site ($^{14}$C$_{NCC, M0072} = \sim$15.5 Kyr; Figure 8). This suggests that thermal degradation of DOM and incorporation of the resulting carbon in carbonates is still ongoing and that the radiocarbon ages of NCC are best explained by a mixture of old DOC, which survives hydrothermal decomposition, and young DOC. The preservation and subsequent leaching of potentially old organic carbon from the basement are supported by recent studies of Lang et al. (2010, 2012), which found that DOC concentration in the vent fluids is almost twice as high.
as those from the seawater. However, the effect of DIC and DOC removal from the oceanic reservoir is not well constrained, and the mechanisms of DOC removal are not well understood (Hansell, 2002).

Our data can be considered to estimate carbon fixation in the oceanic crust. To do this, we use a crustal production rate of $6.0 \pm 0.8 \times 10^{14}$ g/yr calculated by Mottl (2003) and assume that $\sim 20\%$–$25\%$ of the oceanic crust is composed of serpentinitized peridotites (Cannat et al., 1995) so that only $5\%$ of the new seafloor produced per year is composed of ultramafic rocks (Bach et al., 2001). This results in annual storage rates of up to $1.7 \times 10^{13}$ mol C/yr of NCC (avg. $7 \times 10^{12}$ mol C/yr) and up to $6 \times 10^{12}$ mol C/yr of inorganic carbon (avg. $1 \times 10^{12}$ mol C/yr), assuming NCC contents from 39 to 700 ppm and inorganic carbon contents from 14 ppm to 2.4 wt%. Former studies from Alt and Teagle (1999) and Staudigel et al. (1989) estimated storage rates for inorganic carbon of up to $2.7 \times 10^{13}$ mol C/yr, which is approximately half our estimate. Delacour, Früh-Green, Bernasconi, Schaeffer, and Kelley (2008) reported up to $1.2 \times 10^{12}$ mol C/yr for annual storage rates of organic carbon within the oceanic crust, which coincides with results of our studies, and Lang et al. (2006) calculated a global DOC loss of up to $1.2 \times 10^{9}$ mol C/yr through high-temperature axial vents, which accounts for less than $2\%$ of the $\sim 14$ μM DOC loss during deep oceanic circulation. In comparison, our calculation shows 60 times higher DOC removal, which would explain more than the assumed $\sim 14$ μM DOC loss. Thus, moderate temperature and off-axis hydrothermal systems potentially represent an important sink for inorganic and organic carbon compared to high-temperature axis vents.

The NCC content can be used to estimate water-rock ratios during serpentinization. In the Atlantic Ocean, the deeper water column has DOC concentrations ranging from $\sim 41$ to 45 μM/l (average 43 μM/l, Druffel et al., 1992, 2016; Hansell & Carlson, 1998), which corresponds to 0.54 mgC/l. Using the average NCC content of 281 ppm of our study, the calculated water-rock ratio is 520. Previous studies showed that high fluid fluxes and long-lived serpentinization processes are critical for the formation of the LCHF (Delacour, Früh-Green, Frank, et al., 2008). Delacour, Früh-Green, Frank, et al. (2008) used Sr- and Nd-isotopes from drill cores from the central dome and surface samples from the southern wall of the AM to evaluate the water/rock ratios. Using Sr-isotopes and assuming a closed system, they calculated a water/rock ratio of up to 234 and, using Nd-isotopes, a ratio of up to 420,000. Nd isotopes are essentially immobile; thus, the Nd isotope composition of the serpentinitized peridotites usually remains unaffected except at very high water/rock ratios (e.g., Michard & Albarède, 1986). Thus, the significant shift in Sr- and Nd-isotope compositions from mantle compositions in the basement rocks of the AM described by Delacour, Früh-Green, Frank, et al. (2008) provide evidence for high water/rock ratios. Likewise, Boschi et al. (2008) also used Sr-isotopes from samples recovered across the southern wall and the central dome. They calculated water/rock ratios between 100 and 800. Comparing these values shows that our calculated water/rock ratio necessary to explain the NCC content solely derived from circulating seawater is relatively high but in the range of previously calculated values. Due to this, we argue that our results are consistent with very high fluid fluxes beneath the AM.

### 6. Conclusions

This study contributes new data on the geochemistry of inorganic and organic carbon in oceanic serpentinites and gabbroic rocks and provides constraints on the fate of dissolved carbon in seawater during long-lived serpentinization and hydrothermal alteration of the oceanic lithosphere.

The isotopic investigations point to three sources of inorganic carbon: (a) abiotic hydrothermal degradation of DOM; (b) seawater; and (c) mantle volatiles. The relatively $^{13}$C-depleted composition of the organic carbon points to a dominant marine origin with a possible minor component from $\textit{in situ}$ production through microbial activity. Although the biotic formation of organic carbon within the basement of the AM would be possible, there is no clear evidence for significant biological activity in the serpentinites. In contrast, the high carbonate formation temperatures probably inhibited microbial activity. We propose that a high degree of seawater influx channeled below the central part of the southern wall likely favors the transport of marine DOC and DIC into the serpentinites and dominates carbonization at least for the past 38,000 yr. Dispersed carbonates record initial carbonization during the earlier stages of serpentinization and are progressively deposited during continuous hydration and alteration of the OCC. In addition, dispersed carbonates can record an isotopic signature of DOM decay over long geological timescales. Thus, our study suggests that
serpentinites in moderate temperature off-axis hydrothermal systems are important for storage of marine DIC and may represent a more significant sink of DOC from seawater than high-temperature vent systems at mid-ocean ridges.

Moderate-temperature, off-axis hydrothermal vent systems are crucial to better understand the impact of seawater circulation through the oceanic crust on the global carbon budget, and further investigations on oceanic serpentinites and gabbros are necessary to better constrain the amount of carbon removed through deep seawater circulation in the oceanic crust. Furthermore, several authors (Holm et al., 1992, 2006; Martin & Russell, 2007; Shock, 1990; Shock & Schulte, 1998) propose that abiogenic formation of organic compounds necessary for early life requires alkaline conditions and high H$_2$ contents in the hydrothermal fluids. Hydration and serpentinization of mantle peridotites produce these types of conditions; thus, further studies of the transport, transformation, and storage of carbon in these systems will not only help to better evaluate the potential of mantle rocks to store carbon and reduce CO$_2$ emission in the future but may also provide information to better evaluate the conditions of emergence of life on Earth.

## Data Availability Statement

Results of individual analyses of the samples are available online on PANGAEA under the following links: https://doi.org/10.1594/PANGAEA.935276, https://doi.org/10.1594/PANGAEA.935278, https://doi.org/10.1594/PANGAEA.935279, https://doi.org/10.1594/PANGAEA.935357, https://doi.org/10.1594/PANGAEA.935358, https://doi.org/10.1594/PANGAEA.935360.

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