Significance of fluid chemistry throughout diagenesis of aragonitic *Porites* corals – An experimental approach

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Abstract

Marine carbonates are among the most important archives of environmental information in both modern and past environments. Widely used but particularly sensitive archives are the aragonitic skeletons of scleractinian corals. However, due to the metastable nature of aragonite, a multitude of chemical, mineralogical, and (micro) biological processes can lead to diagenetic alteration of these archives and their proxy information can be altered or lost. Here, hydrothermal alteration experiments were performed to create a better understanding of the diagenesis of an often-utilized genus, *Porites*. Same-specimen subsamples were heated in two fluid types and at two temperatures and durations, and their resulting alteration features were assessed to allow insight to the mechanisms and drivers of diagenetic modification. Experiments with fluid temperatures of 130°C induced remobilization and darkening of organic matrices, with no other evidence for alteration observed. In contrast, specimens exposed to a temperature of 160°C underwent significant diagenetic alteration dependent on fluid type. Fluid chemistry, particularly Mg/Ca ratios, was found to regulate the type of alteration (e.g. neomorphism or reprecipitation). Reaction with meteoric water resulted in almost complete neomorphism of the aragonite skeleton to blocky calcite, as well as significant exchange with the experimental fluid. In comparison, samples altered in the experimental burial fluids record no mineralogic or significant isotopic change, but instead, small-scale dissolution–reprecipitation of the primary skeleton, along with the precipitation of pore-filling aragonitic needle cements was observed. The δ^{18}O carbonate data indicate transformation via dissolution–reprecipitation mechanisms depending on the degree and mechanism of diagenesis, and are strongly dependent on fluid chemistry. The main outcome of this work is that a multi-proxy approach has the best potential to shed light on the interpretation of processes and pathways of aragonitic coral alteration. This study has implications for early alteration of carbonate archives within varying diagenetic fluids, with results aiding in the identification of past burial conditions.

**KEYWORDS**

Aragonite, Carbonates, corals, diagenesis, isotope geochemistry, palaeoenvironment.
1 INTRODUCTION

The fairly acute response of Aragonitic corals to environmental conditions leads to their use as archives of their depositional environment, particularly sea-level, temperature, and water chemistry. The common carbonate archive, *Porites* sp., corals, have been extensively documented in the literature (Pätzold, 1984; Allison, 1994; Stanley & Swart, 1995; Alibert & McCulloch, 1997; Emnar et al., 2000; Felis, Patzold, & Loya, 2003; McGregor & Gagan, 2003; Al-Rousan, Felis, Manasrah, & Al-Horani, 2007; Hendy, Gagan, Lough, McCulloch, & DeMenocal, 2007; McGregor & Abram, 2008; Benzerara et al., 2011; Motai et al., 2012; Lazareth et al., 2016; Casella et al., 2018). Due to the geographical range of *Porites* sp., it has been found to primarily record environmental information in tropical and subtropical regions (Schlager, 2005; Veron et al., 2009; Milliman, Muller, & Forstner, 2012). Therefore, the chemical composition of the coral skeleton can be calibrated to environmental parameters such as isotopic signatures (Emiliani, Hudson, Shinn, & George, 1978; Swart, 1983), elemental concentrations (Gothmann et al., 2015; Stolarski et al., 2016; Giri & Swart, 2019), seasonality (Dunbar & Wellington, 1981), temperature (Carricart-Ganivet, 2004; Rosinski & Walsh, 2016), salinity (Coles & Jokiel, 1978; Corrège, 2006), and pH (Pelejero et al., 2005). Furthermore, the chemical composition can provide a good basis for identifying changes to the textural and geochemical composition of the corals. The (isotope)geochemical proxy approach to corals and other marine carbonate archives is increasingly challenged because studies on diagenesis reveal that mineralogical, chemical, and biological alteration may begin relatively early in the burial history, or may even affect biominerals during the lifetime of an organism and/or in post-sedimentary environments (Murra, Gagan, & McCulloch, 2001; Lazar et al., 2004; Lazareth et al., 2016). Evidence for this alteration primarily comes from patterns in biomimeral microstructure (Cusack et al., 2008; Rollion-Bard, Mangin, & Champenois, 2009) or trace element ratios (Meibom et al., 2004; Hathorne et al., 2013) that deviate from primary signatures in the aragonitic biomimeral. As in most carbonates, the fundamental problem with a given fossil coral skeleton and its archive data is that the present state of the sample often reflects a complex biomimeralization (Allemand et al., 2004; Tambutté et al., 2011) and alteration history that is often not easy to reconstruct.

A non-classical crystallization concept discussed by Cölfen & Antonietti (2008) describes nanoparticulate intermediates during the formation of biominerals. In lieu of the classical crystallization model that describes a purely inorganic process where layers of ions are deposited on crystal nuclei, the non-classical model prefers an organically influenced mechanism involving colloidal pathways and mesocrystallization. This results in an “organic-inorganic hybrid structure” (Cölfen, 2010) composed of small regions connected by organic compounds around and within the crystal. This non-classical model has been more recently observed by other authors (Cartwright, Checa, Gale, Gebauer, & Sainz-Díaz, 2012; Marin, Le Roy, & Marie, 2012; Jin, Jiang, Pan, & Tang, 2018) confirming the presence of organic molecule and precursor phases during the formation of biominerals. The presence and influence of organic molecules during the mineralization process have also been identified in corals, and can be species specific (Reggi et al., 2014). This skeletal organic matter can be an indicator of not only the mineralization process, but can also aid in the detection of early alteration processes, as they are generally more reactive than their inorganic counterparts. Evidence for this can be observed by the contraction of the aragonite unit cell following annealing due to the removal of organic matter (DeCarlo, Ren, & Farfan, 2018) which coats the aragonite crystals (Clode & Marshall, 2002). As organics can be a source of internal fluids, and inherently respond differently than inorganic components, the presence of these internal organics in carbonate archives can greatly affect the response of the system during alteration.

In order to better understand the diagenetic timing, processes, and products of aragonitic corals, hydrothermal alteration experiments were performed under controlled conditions on specimens of *Porites* sp. To evaluate the impact of different diagenetic fluid types on fluid-solid interactions and resulting alterations of petrographic and geochemical proxy data, four diagenetic scenarios (two environments and two durations) were simulated. Specifically, the focus of the research is on: (a) aragonitic coral skeletons that become exposed to meteoric diagenetic fluids (due to processes such as relative sea-level fall) and (b) corals that undergo marine burial and are exposed to marine diagenetic fluids. It is emphasized that these experiments and the fluids cannot mimic the complex processes active in natural alteration pathways, but rather aim to reproduce a simplified model setup of alteration features observed in naturally altered corals. As organics can be a source of internal fluids, and inherently respond differently than inorganic components, the presence of these internal organics in carbonate archives can greatly affect the response of the system during alteration.
are placed in context with naturally altered material, and alteration patterns in (isotope)geochemical and ultrastructure are discussed. Data shown here are relevant for those concerned with diagenetic processes of aragonite minerals, and proxy preservation of carbonate archives during different alteration pathways.

2 | MATERIALS AND METHODOLOGY

For this study, an adult Porites species coral specimen was collected in 2014 from a reef at Society Island (French Polynesia) in mean tidal water depths between two and five metres, with seawater surface temperatures ranging from 28.9 to 26.7°C throughout the year (Global Sea Temperatures, 2019). The coral specimen (Figure 1A) was cut in half using a diamond saw blade, and then further cut into subsamples ca. 2 × 1 × 1 cm in length. Four subsamples (labelled with stars, Figure 1B) were chosen from the coral specimen for the alteration experiments. An additional subsample (Figure 1C; CHA-K-002-B5) was used as pristine reference sample for comparison and calibration of alteration features.

2.1 | Experimental alteration protocol

The method applied here follows the experimental protocol described in detail in Ritter et al. (2017). Hydrothermal alteration experiments were performed at the Institute of Applied Geosciences at Graz University of Technology, Austria. Four Porites sp. subsamples were placed in individual stainless-steel Teflon-lined containers (Figure 1D,E) containing 25 ml of artificial diagenetic fluids produced in the laboratory. The two fluids used in this study are the same as those used in Pederson et al. (2019), and include: (a) meteoric water (10 mM NaCl) and (b) burial fluid (100 mM NaCl + 10 mM MgCl₂). These fluids were chosen because of the frequency with which coral skeletons enter the meteoric diagenetic realm during relative sea-level fluctuations, and alternatively, their exposure to shallow burial fluids. Given that burial fluids may include a wide range of chemical compositions, a modified seawater-type of fluid was used (herein referred to as “burial fluid”) that was Ca-lean at the beginning of the experiment. The extreme undersaturation of the experimental fluid with regard to Ca induced rapid initial dissolution and triggered reactions. All fluids were spiked with a 1:10 mixture of ¹⁸O-depleted H₂O (IASON) laboratory reference water [δ¹⁸O = −395‰, Vienna Standard Mean Ocean Water (VSMOW)] and local deionized water, to easily recognize fluid-mineral isotope exchange. The mean oxygen isotope ratios of both reactive fluids are in the order of −47‰. The containers were then placed in an oven and exposed to 130 and 160°C for either 4 or 8 weeks depending on the specimen (Figure 1E; Table 1). The authors acknowledge that neither meteoric nor burial fluids reach these temperatures in natural systems. Relatively high fluid temperatures were used to effectively increase the reaction rate, with the aim to induce diagenetic alteration products comparable to those found in naturally altered systems. Following the hydrothermal experiments, the autoclaves were removed from the oven and cooled to room temperature. Samples were removed and dried at 40°C overnight. The post-experimental fluids were filtered with a 0.2 μm cellulose acetate filter and stored for further analyses. For post-alteration data collection, the hydrothermally altered samples were cut in halves (ca. 1 × 1 × 0.5 cm) using a steel saw blade. One half was used for thin section preparation, and the other was kept for additional geochemical analyses.

**FIGURE 1** Experimental preparation and alteration procedure. (A) Unaltered, pristine Porites sp. coral sample. (B) 23 subsamples, with the stars indicating those used for the hydrothermal alteration experiments in this study. (C) Close-up photograph of the pristine sample. (D) Schematic of sample within a stainless-steel autoclave container. (E) Oven in which sample autoclaves were placed for the duration of the experiment.
|                          | Unaltered, pristine sample | 130°C meteoric | 160°C meteoric | 130°C burial | 160°C burial |
|--------------------------|----------------------------|----------------|----------------|--------------|--------------|
| Sample name              | B5                         | A1-8           | A1-5           | A1-7         | A1-2         |
| Experimental duration (weeks) | —                          | 8              | 4              | 8            | 4            |
| Mineralogy               | 97.2% Ar                   | 98.7% Ar       | 99.1% Cc       | 98.9% Ar     | 99.1% Ar     |
| Framework textures       | Fine Ar needles (<5 µm)     | Precipitation and recrystallization, feathery Ar crystals and meniscus cementation | Precipitation and recrystallization, large isometric crystals (Cc rhombohedra) | Precipitation and recrystallization, fibrous Ar needles and granular cementation | Precipitation and recrystallization, Ar needles infilling pore space |
| Pore space (%)           | 25                         | 23             | 38             | 28           | 35           |
| Organic matter (FL)      | Homogenous and at rims      | Centered       | Centered and accumulated in portions | Centered | Centers, lower sample margin and patchy accumulations |
| Elemental distribution   | Mg enriched to centers, Sr homogenous and depleted at connection bridges, S ↑ slightly to centers | Mg ↑ alternating to centers, Sr homogenous and depleted to rims, S ↓ but homogenous | Mg ↓ and cements ↑, Sr and S ↓ in cements | Mg ↑ in cements and centers, Sr homogenous and ↓ in cements, S ↓, but homogenous | Mg ↑ in cements, Sr ↑ in cements, S ↓ in cements |
| Drilled δ¹⁸O (average)   | −4.2‰ (n = 33)             | −7.2‰ (n = 81) | −49.0‰ (n = 46) | −6.8‰ (n = 85) | −6.6‰ (n = 47) |
| Drilled δ¹³C (average)   | −1.9‰ (n = 33)             | −2.7‰ (n = 81) | −0.8‰ (n = 46) | −0.3‰ (n = 85) | −0.8‰ (n = 47) |
| SIMS δ¹⁸O (min., max., av.) | —                          | —              | −66.1, −3.5, 40.5‰ (n = 36) | —           | −18.9, −5.0, −13.3‰ (n = 20) |

Ar, aragonite; Cc, calcite.
2.2 | Powder X-ray diffraction

Powder X-ray diffraction (PXRD) was used to determine the mineralogy of the five subsamples (including the unaltered and four hydrothermally altered samples). To quantify the carbonate minerals present, aliquots of powder samples were drilled from the remaining thin section epoxy plugs, either by hand using a Dremel, or with a computer-controlled milling device (CAM 100, vhf, Ammerbuch, Germany). Samples of ca. 80 mg were collected and homogenously distributed on a silicon sample carrier, mounted and aligned on a rotating goniometer head. The PXRD measurements were performed on a PANalytical EMPIREAN diffractometer using copper radiation ($\lambda_1 = 0.154$ Å) equipped with a PIXcel$^{1D}$ detector (Medipix2 collaboration, Ruhr-University, Bochum, Germany). Scanning range was 5–80° 2-Theta, with a step size and duration of 0.0131° and 598.9 ms respectively. Phase analyses were carried out using the software package MATCH! – Phase Identification from Powder Diffraction (version 3.6.2.121), and performed with a Rietveld refinement and mineralogy data from De Villiers (1971; for aragonite) and Graf (1961; for calcite).

2.3 | Microscopy

2.3.1 | Light and fluorescence microscopy

Thin sections of both pristine and experimentally altered samples were investigated by means of light microscopy in normal, transmitted, and polarized settings (Leica DM4500P; Leica Microsystems GmbH, Wetzlar, Germany) to determine the textures of the skeletal framework, and to identify diagenetic features. Pore space was calculated by creating grey-scale histograms using the software GIMP (Version 2.8.22). Organic matter distribution was observed via fluorescence imaging with a Leica EL6000 external light source coupled to the microscope to obtain an initial evaluation of the degree of diagenesis (Boto & Isdale, 1985; Ramseyer et al., 1997). Best results were achieved using a blue light filter which yielded bright green fluorescence images of the analysed Porites sp. samples (filter set I3 for blue light excitation: 450–490 nm, emissions 515 nm). The voltage of the light source varied between 100 and 240 V and a frequency of 50 to 60 Hz.

2.3.2 | Scanning and field electron microscopy

Scanning electron microscopy (SEM) was used to further investigate crystal morphology, textures, and fabrics. Thin sections of Porites sp. were coated with a thin carbon layer and investigated using a LEO/ZEISS Gemini 1530 SEM (Carl Zeiss AG) with an accelerating voltage of 20 kV and a beam current of 1.6 nA. Crystallographic data was collected using electron backscatter diffraction (EBSD) for Porites sp. samples exposed to 160°C. These were investigated for their visible alteration identified with optical and mineralogical analyses. Crystal orientation of the investigated samples was determined by EBSD (Nordlys detector by Oxford Instruments). The data acquisition and analyses were performed using the software packages AZtec and Channel 5 (Oxford Instruments). Grain detection boundary conditions were set at a 10° maximum misorientation of crystal axes, with a map processing of 3.5 μm steps. The field-emission scanning electron microscope (FE-SEM, Merlin Gemini II by ZEISS) was operated in high-resolution mode, with a beam energy of 20 kV, sample current of 400–500 pA, working distance of 25 mm, and tilt angle of 70°.

2.4 | Electron microprobe

A Cameca SXFiveFE microprobe was used to obtain element distribution maps from the five Porites sp. samples. The spatial distribution of the Sr, Mg and S was recorded (800 × 800 px section for 130°C samples, and 1,024 × 1,024 px section for the unaltered and 160°C samples) and compared to identify changes in organic matter and mineralogy. Data are displayed using a rainbow colour scale showing relative differences in the elemental X-ray intensities. The analytical settings used were set to an acceleration voltage of 15 kV for all sample types, while the electron beam current was 79 nA for the 130°C samples and 255 nA for the unaltered and 160°C samples. All maps were acquired with a step width of 1 μm, and a dwell time of either 40 ms (130°C samples) or 35 ms per pixel (unaltered sample, and 160°C samples).

2.5 | Carbon and oxygen isotope data of drilled bulk material

The remaining sample plugs from the thin section preparation were mounted on an aluminium plate using glue and were drilled using a micromill device for isotopic bulk compositions (computer-controlled device—CAM 100, vhf, Ammerbuch, Germany; manually operated—Sherline Deluxe 5400; Vista). Sample aliquots were drilled with a width of 4.0 mm and a depth of 0.7–1.2 mm. Distance between sample transects was 100 μm. Samples, ranging in weight between 30 and 50 μg, were loaded into 4.5 ml round-bottomed borosilicate vials, capped with Labco butyl rubber septa, and weighed using a Mettler Toledo XPR6UD5 microbalance. Sample vials were then put in an oven (ca. 105°C) for 24 hr to dry, and then a desiccator for subsequent cooling to room temperature. The vials were placed in an aluminium tray and flushed with He at 70°C (Spoetl & Vennemann, 2003). Samples were run in the geochemistry and stable isotope laboratory at Ruhr-University Bochum using a Gasbench II equipped
with a GC autosampler and coupled to a ThermoFinnigan MAT253 mass spectrometer (Thermo Fischer Scientific). On average, 10 drops of P₂O₅ (density 1.92 kg m⁻³) were added to each aliquot, and the CO₂ was measured for its carbon and oxygen isotopic composition in a continuous flow mode. Carbonate standards CO1, CO8, NBS18, NBS19, IAEA603 and an internal standard (ISO-A) were used to normalize the data, with a standard deviation of 0.04–0.12‰ and 0.01–0.04‰ for δ¹⁸O and δ¹³C respectively. Corresponding δ¹⁸O and δ¹³C values are given in‰ relative to the Vienna Pee Dee Belemnite (VPDB) standard.

2.6 | Oxygen isotope measurements by secondary ion mass spectrometry

The Porites sp. samples exposed to reactive fluids at 160°C were chosen for additional oxygen isotope analyses with secondary ion mass spectrometry (SIMS) based on the greatest observed alteration. Measurements were performed at CRPG-CNRS (Nancy, France) using a CAMECA IMS 1280. Details of the technique are described in Rollion-Bard et al. (2007). A primary beam of Cs⁺ ions with an intensity of ca. 4 nA was focused to a spot of approximately 15 µm, with an entrance slit of 100 µm, and a field aperture of 2,500 µm. The multicollector slit was 500 µm, resulting in a mass resolving power (M/M) of ca. 4,500, completely resolving the interference peaks of ¹⁶OH₂, ¹⁷OH and ¹⁶OD. Measurements were conducted in multicollection mode using two off-axis Faraday cups (L'2 and H1), and a fully opened energy window. The typical acquisition sequence of each point consisted of 60 s of presputtering, followed by 30 cycles of 5 s measurements. During the presputtering, the backgrounds of the Faraday cups were measured. Typical intensities of about 5.5 × 10⁶ counts/s are measured on the ¹⁸O⁻ peak. Two in-house standards (calcite CCcgA and aragonite Arg) were used for the correction of the interference of the instrumental mass fractionation (IMF), due to the difference of IMF between aragonite and calcite (Rollion-Bard et al., 2007). An external reproducibility of ±0.26‰ (at the 1σ level) (CCcgA) and ±0.20‰ (Arg) was observed, with internal precision generally better than ±0.1‰. The total error for each analysis is the quadratic sum of the reproducibility and the internal precision. All δ¹⁸O values are expressed relative to the international standard VPDB.

3 | RESULTS

A short description is provided here of the main aspects of the data collected in this study from the pristine sample, with the remainder of the section relating to the hydrothermal alteration experiments. The pristine coral sample (Figure 2A) used in this work displayed a typical primary aragonitic mineralogy (Table 1; Figure 3) and framework (Figure 4A,B), including a uniform pore space (25%). The primary skeleton is composed of elongated, partly radially growing crystals, infrequently covered by rounded grains approximately 20 µm in diameter, and <5 µm fractures and voids. The centres of the coral fabric show larger aragonite crystals (~150 µm in diameter), with smaller aragonitic needles (<5 µm) along the rims of some pore space. Thin lines were observed within the skeleton, which are assumed to be primary growth lines. Organic matter is generally homogenously distributed (Figure 4C), with a slightly greater amount observed at the rims of the coral fabric along organic-rich growth lines, and within some small (<30 µm) organic-rich inclusions. A homogenous distribution of Sr was observed, but relatively higher amounts of both Mg and S were seen towards the centre of the coral framework. Average δ¹³C and δ¹⁸O values are 1.9 ± 0.07‰ and −4.2 ± 0.04‰ respectively (Table 1).

3.1 | Mineralogy

Based on PXRD and EBSD analyses, all subsamples remained aragonitic, with the exception of the sample exposed to meteoric fluids at 160°C (Figure 2), in which a transformation from aragonite to low-Mg calcite was...
observed (Figures 3 and 5; Table 1; 98.3% calcite and 1.7% aragonite).

3.2 | Textures and organic distribution

Independent of the alteration conditions, optical microscopy revealed an alteration of the original coral framework, including: organic degradation and redistribution, mineral dissolution, changes in crystal size and morphology, and cementation. Generally, the samples exposed to meteoric reactive fluids display neomorphism of the original crystal structure, whereas infilling cementation occurred predominantly in the samples altered in burial fluids.

3.2.1 | Samples exposed to meteoric reactive fluids at 130 and 160°C

In the subsamples exposed to a meteoric reactive fluid at 130°C (Figure 2B), minor textural changes were observed, with small amounts of recrystallization and dissolution at the fringes of original pore spaces (Figure 4D). Pore space was determined to be 23% (Table 1). Secondary crystals, about 100 μm in size, were observed within the sample (Figure 4D), with a higher amount towards the outer fringe of the sample, indicating recrystallization. Under the SEM, the sample displays many similarities with its unaltered counterpart, but contains bridges connecting the coral skeleton, with skewed feathery needles <5 μm along one side of the bridge, and small (<5μm) blocky crystals on the other (Figure 4E). Although blocky cements can form at the bridges within the framework, aragonite mineralogy was retained (Figure 3; Table 1). Slightly higher fluorescence suggests a weak degree of mobilization of organics from the outer portions of the coral framework (Figure 4F).

The subsamples exposed to a meteoric reactive fluid (Figure 2C) at 160°C displayed the highest amount of textural alteration. Within the coral framework, portions of the initial skeleton were dissolved, and pore space increased to 38% (Table 1). Alteration fabrics include neomorphism, with large isometric-shaped calcite crystals with diameters ranging from 150 to 300 μm (Figure 4G,H). Meniscus cements (>250 μm) with a circumgranular blocky fabric with partly bladed appearances connect the primary coral skeleton (Figure 4G). High amounts of diagenetic cements often occur at the sample rim, and near the organic-rich regions. The SEM images evidence both slight dissolution and neomorphism (Figure 4H). The dissolved portions are found at the outer margins, and along vertical channel-shaped (intergranular) cavities. The newly formed blocky to granular crystals are approximately 20 μm and have a reduced fluorescence (Figure 4I). In some portions of the sample, cements fill intergranular and intraskeletal pores. Some of the voids between the newly formed cements show peloidal microcrystalline cements (10 μm), as well as an isopachous crust in some pores, while blocky to granular cements are generally found throughout the sample. Crystallographic features from the EBSD map show large (up to 250 μm in diameter), randomly orientated, blocky calcite grains (Figure 5A). Increased fluorescence

**FIGURE 3** PXRD measurements of the pristine, 130 and 160°C samples. The 160°C meteoric sample shows a clearly visible calcite peak indicating the largest mineralogical change observed in this study. Ar = aragonite, Cc = calcite
towards the centre of the coral framework (similar to the pristine sample) was observed (Figure 4I), but patchy accumulation of dark organic matter towards the sample margins may indicate degradation (Figure 2E).

3.2.2 | Samples exposed to burial reactive fluids at 130 and 160°C

The sample exposed to a burial-type fluid at 130°C generally remained texturally unaffected for the duration of the experiment (Figure 2D). The framework consists of elongated 100 μm fibrous-shaped and blocky aragonitic crystals (Figure 4J). Some small areas showed dissolution features, with 28% pore space (Table 1). Gravitational, granular cements (70–100 μm) partially fill the round intergranular cavities (maximum 250 μm diameter) within the coral fabric and within some of the connection bridges (Figure 4J). The SEM images also reveal a similar coral framework as the unaltered sample, but with small dissolution features (<10 μm diameter voids) seen throughout the sample (Figure 4K). Additionally, a distinct, needle-like cement (up to 10 μm in length) was observed along the pore space. A redistribution or removal of organic matter was not clearly visible under normal or transmitted light, but some randomly distributed rounded accumulations dark brown in colour (<50 μm in size) were observed at the sample rims (Figures 2D and 4J).

FIGURE 4  Thin section (left column), SEM (middle column), and fluorescence images (right column) showing internal textures and organic matter (OM) distribution in the unaltered and altered samples. (A–C) Unaltered sample showing typical skeletal morphology (A, B), and slightly higher OM at the skeleton rims (C). (D–F) The sample altered at 130°C in meteoric fluid, showing minor amounts of recrystallization within the coral skeleton (D), but a primarily unaltered structure despite skewed feathery needles <5 μm along one side of the connecting bridge in the skeleton (D). (F) Here, OM is slightly higher towards the center of the coral framework. (G–I) The sample altered at 160°C in meteoric fluid showing large calcite crystals indicating neomorphism (G), with evidence of dissolution and recrystallization, as well as large blocky calcite cements occurring at the skeleton rims (H). (I) OM is highest towards the center of the coral framework, as well as patchy accumulation towards the skeleton margin, with the lowest amounts in the blocky cements. (J–L) The sample altered at 130°C in burial fluid, showing generally unaltered textures (J, K), and OM enriched at the skeleton rims and in elongated fractures within the skeleton (L). (M–O) The sample altered at 160°C in burial fluid showing newly formed radially-growing fibrous needle cements infilling the pore space (M), which grow normal to the coral fabric and infilling the pore space (N). (O) OM is enriched towards the center of the primary skeleton and depleted in the fibrous cements.
Brighter fluorescence was observed along the boundaries of the pore space within the coral framework, with the centres of the coral fabric containing 100 μm patches and elongated fractures of light fluorescence patterns (Figure 4L). The sample exposed to a reactive burial fluid at 160°C displayed a lower amount of neomorphism within the framework (Figure 2E) compared to its meteoric counterpart. Here, newly formed radially-growing fibrous needle cements (<60 μm) occur throughout the sample, infilling the primary pore space (35%) (Table 1), resulting in isopachous crusts within the pores (Figure 4M). The SEM images further indicate precipitation features throughout the sample, with <10 μm voids in the primary coral framework, and seemingly well-preserved connection bridges (Figure 4N). Elongated 20 μm-sized acicular to fibrous cements grow normal to the coral fabric and infill the pore spaces, showing significant length elongation generally parallel to the c-axis. Organic matter is enriched towards the centre of the non-recrystallized skeleton, as well as the lower margin of the sample, with a reduced fluorescence in the diagenetic cements (Figure 4O). The EBSD data (Figure 5B) confirms the textural results, showing aragonitic mineralogy of the primary coral skeleton, and fibrous shaped, pore-filling aragonite needles, up to ca. 100 μm in length (Figure 5B).

### 3.3 Elemental distribution

#### 3.3.1 Samples exposed to meteoric reactive fluids at 130 and 160°C

The subsample exposed to meteoric fluids at 130°C shows a similar elemental distribution compared to the pristine sample, with homogeneous Sr concentrations throughout the skeleton (Figure 6F), as well as relatively higher amounts of Mg towards the centre of the coral framework (Figure 6E). The major difference is with the distribution of S where, instead of increased amounts towards the centre of the skeleton, a homogenous distribution was observed (Figure 6D). The sample exposed to 160°C in meteoric fluids displays striking differences, with a redistribution of organics (S) and major Ca-substituting ions (Sr and Mg) (Figure 6G through I). A major difference between the neomorphosed blocky calcite of the primary skeleton and the bridge and cements that connect the blocky crystals was observed. The neomorphosed bridge cements are characterized by relatively higher amounts of Mg (Figure 6H), but lower amounts of Sr and S (Figure 6G through I), which are also relatively low in the rim cements around the primary framework.

#### 3.3.2 Samples exposed to burial reactive fluids at 130 and 160°C

The sample exposed to burial fluids at 130°C has relatively high amounts of Mg towards the centre of the skeleton, similar to the pristine sample. However, the highest amounts of Mg occur within the thin grain bridges (Figure 6K). Similar to the 130°C meteoric sample, S has been relatively reduced and has a homogenous distribution (Figure 6J). Sr distribution remained relatively unaltered (Figure 6L). Similar to the sample altered at 160°C in a meteoric fluid, the coral exposed to a burial fluid at 160°C displays the greatest differences between the primary coral structure and the diagenetic cements. Within the inner portions of the primary framework, relatively higher amounts of Mg and S were observed (Figure 6M,N), similar to the pristine sample (Figure 6A,B). The pore-filling cements are characterized by the highest amounts of Mg and Sr, but the lowest amounts of S (Figure 6M).

### 3.4 Isotopic composition

#### 3.4.1 Samples exposed to meteoric fluids at 130 and 160°C

A larger range and more negative values for both δ¹³C and δ¹⁸O were observed in the samples originating from the drilled transects of the 130°C meteoric sample compared to the pristine (Table 1; Figure 7A,B). Carbon isotope values range from −2.0 to −3.5‰ (average −2.7 ± 0.04‰, n = 81), with the most negative values measured towards the centre.
of the sample, opposite of the trend seen in the pristine specimen. The $\delta^{18}O$ values ranged from $-6.0$ to $-7.8\%e$ (average $-7.2 \pm 0.08\%e$, $n = 81$), which is ca. $3\%e$ more negative than the value for the pristine counterpart, with no detected trend between the outer and middle portions. Within the sample altered at $160^\circ C$ in meteoric fluid, $\delta^{13}C$ and $\delta^{18}O$ values range from $-0.4$ to $-2.0\%e$ (average $-0.8 \pm 0.03\%e$, $n = 46$) and $-31.0$ to $-58.9\%e$ (average $-49.0 \pm 0.16\%e$, $n = 46$), respectively (Figure 7C). With the overall lowest $\delta^{18}O$ values of all specimen, the most negative values in transects generally occur towards the middle of the sample and the lower outer rim, where the most negative $\delta^{13}C$ values were also observed. The SIMS $\delta^{18}O$ measurements ($n = 38$) displayed a much larger range of values from $-3.5$ to $-66.1\%e$ (Figure 8A). The isotope variation reveals a relatively regular fluctuation along the examined outer margin. Significantly less-negative values were observed within areas with relatively darker colours (spots 5, 10, 12, 28 and 31), suggesting higher organic matter, and lower amounts of recrystallization. In contrast, the remaining points have more negative $\delta^{18}O$ values, and correspond to visually more transparent colours, and higher amounts of blocky cementation.
3.4.2 | Samples exposed to burial fluids at 130 and 160°C

The samples originating from the drilled transects of the 130°C *Porites* sp. sample exposed to the burial fluid ranged in δ¹³C and δ¹⁸O values from +0.5 to −1.4‰ (average −0.3 ± 0.04‰, n = 85) and −6.0 to −8.3‰ (average −6.8 ± 0.08‰, n = 85) respectively (Figure 7D). The most negative values were observed towards the lower outer rim of the sample. Transects analysed from the sample exposed to 160°C have well-correlating trends in δ¹³C and δ¹⁸O values (Figure 7E) and are significantly less negative compared to the samples exposed to meteoric fluids at 160°C. With δ¹³C and δ¹⁸O values ranging from +0.7 to −2.3‰ (average −0.8 ± 0.04‰, n = 46) and −5.3 to −8.2‰ (average −6.6 ± 0.07‰, n = 46) respectively, the most negative values were observed towards the centre and outer margins of the sample. The SIMS δ¹⁸O analyses (n = 27) along the lower margin ranged from −5.0 to −19.0‰ (Figure 8B), with more positive values (−7.5 ± 2.5‰) occurring along the left side margin within the fibrous cements, as well as within the main coral framework (spots 1–6). More negative values (−15.0 ± 3.5‰) were primarily observed within >0.25 mm of the lower margin (spots 7–27) (Figure 8B).
INTERPRETATION AND DISCUSSION

4.1 ‘Early’ diagenesis: Textural and elemental alteration

With the exception of minor surficial alteration features, the aragonite mineralogy and coral skeleton structure were visibly not affected by the 130°C alteration experiments, regardless of fluid type. This outcome could be strongly influenced by the relatively short experimental duration (8 weeks). It is assumed that if these samples were exposed to reactive fluids at 130°C for months to years, a significant degree of alteration would have been observed. Hence, by referring to “early” diagenesis, reference is made to the fact that under these specific experimental conditions, reaction rates are comparably slow and only weak alteration features are observed. Compared to the unaltered, pristine *Porites* sp. sample, which contained small aragonite crystals throughout the skeleton framework, the samples exposed to 130°C meteoric and burial fluids displayed a minor increase in crystal size, primarily along the pore space walls (Figure 4C,G). Although this change may indicate dissolution–recrystallization processes, X-ray diffraction analyses of the sample altered at 130°C revealed a mineralogical retention of >98% of the original aragonite (Figure 2), confirming the minimal extent of alteration or, alternatively, a recrystallization of biogenic aragonite to form abiogenic aragonite.

Element distribution maps indicate elemental redistribution under increasing temperature (Figure 6). Elemental abundance of Sr, Mg and S were found to be the best indicators of alteration. Within the lowest temperature (130°C) experiments, Sr and Mg maps—used here to indicate a mineralogical change—suggest moderate or no alteration relative to the pristine *Porites* sp. sample. Magnesium showed alternating relatively higher and lower amounts in the pristine sample with slightly increasing concentrations towards the centre of the coral framework (Figure 6B). Similar distribution patterns were observed in the 130°C meteoric sample (Figure 6D through F), with a general preservation of alternating layers still visible in some places. Whereas relatively no difference was observed within the meteoric sample, the burial sample provided the first evidence of redistribution of Mg (Figure 6K). These were mainly observed within the bridges between the primary framework, indicating a possible exchange of Ca$^{2+}$ or Sr$^{2+}$ ions with Mg$^{2+}$. As the burial fluids contain much higher concentrations of Mg, this exchange would be plausible. Although textural data does not suggest recrystallization of the burial samples at the lower temperatures, small-scale, volume-by-volume dissolution–recrystallization processes likely resulted in the higher Mg concentrations observed. This is especially plausible within the thin bridges, which would have been extremely susceptible to diagenesis due to their high fluid-to-volume ratios.

Another indication of early diagenesis occurred within the organic matter of the coral framework. Due to the various controls and influences on organic matter during the secretion of coral skeletons (Morse, Arvidson, & Lüttge 2007; Swart, 2015), including (but not limited to) metabolisms of algae, fungi, bacteria or other boring organisms, temperature, pH, and freshwater input, the authors cannot definitively rule out the effects of inherent variability within the samples. However, the effects of these aforementioned processes on organic matter during deposition are not the focus of this work, and since the investigation of the unaltered sample contained no indications of early diagenesis, it can be assumed that any
differences observed are a result of the experiment. In this study, changes to organic matter can be insinuated using light microscopy and elemental data. However, fluorescence microscopy has been used to observe organic distribution, functionality, effect on mineral growth, and even the molecular structure (Ramseyer et al., 1997; Wanamaker et al., 2009). In this study, it was primarily used to evaluate the removal or mobilization of organic compounds within the coral samples during hydrothermal alteration. Dark colours, or even non-fluorescence, suggest organically-depleted portions in the coral skeleton, whereas bright fluorescence suggests higher concentrations (Wanamaker et al., 2009). The unaltered, pristine sample primarily displayed homogeneous fluorescence, with slightly brighter green fluorescence at the rims (Figure 4A). Within the 130°C experiments, fluorescence images indicate a slight redistribution of organics, with a relatively higher concentration towards the centre of the coral skeleton compared to the pristine sample (Figure 4C,F). The authors suggest that this indicates an initial depletion of the organics beginning with the outer portions of the skeleton. This is a likely scenario due to the movement of fluids from the outer pore walls which are more exposed to the diagenetic fluids, towards the sample centre. These results document a differentiation of early diagenesis between inorganic and organic matter, where the earliest alteration response is observed within the organic constituents, and the inorganic (crystalline) components are generally unaffected.

This early alteration of the organic constituents was also indicated by changes in the distribution of S (Figure 6), which has a strong association with various organic compounds (Fichtner et al., 2018). Previous work documented that S compounds in the skeleton of corals are present both as SO₄²⁻ and organic S in the coral tissue that surrounds the polyps (Cuif, Dauphin, Doucet, Salome, & Susini, 2003). These results suggest the disintegration of S-containing organics. The S maps indicate a generally even distribution throughout the coral skeletons for the samples treated at 130°C, with a slightly higher amount towards the centre of the skeleton (Figure 6D,J). Although organic matter has been shown to not fully decompose below 150°C conditions in related experiments (Jonas, Muller, Dohmen, Immenhauser, & Putlitz, 2017; Ritter et al., 2017), this initial removal of organic matter corresponds well to findings of other studies of biogenic samples that have shown decomposition to begin at temperatures around 100°C (Gaffey, 1988; Gaffey, Kolak, & Bronnimann, 1991). The type and size of organic molecules, and the duration of exposure to heat are also relevant as different compounds exhibit different degradation gradients and pathways (Mohamed, Yusup, & Maitra, 2012). Under relatively slow, long-term (10⁷–10⁸ years) heating conditions, the disintegration of reactive organic compounds begins around 60°C (Petrova, Mahlmann, Stern, & Frey, 2002; Mahlmann & Le Bayon, 2016). Within the scope of the experimental alteration discussed here, these results likely indicate the early removal of intraskeletal organic matrices, which can be related to biomineralization and diagenetic pathways in natural settings.

4.2 | ‘Later stage’ diagenesis: Cementation and recrystallization

Despite a shorter experimental duration (4 versus 8 weeks), the higher temperature in the 160°C experiments resulted in higher rates and more extensive diagenesis of the Porites sp. samples for both fluid types. As reaction rate constants generally double for a corresponding increase of 10°C (see above), it is predicted that the increase of 30°C should result in much higher reaction rates and degree of alteration regardless of the shorter experimental duration. Extensive alteration of textures, mineralogy, and organics was observed, and is primarily attributed to “later stage” alteration, perhaps an analogue of meteoric and burial diagenesis, driven by dissolution–reprecipitation processes and mineral solubility. The initial Ca-lean nature of the experimental fluids resulted in a significant fluid–solid disequilibrium causing rapid dissolution. This disequilibrium is not an accurate simulation of natural diagenetic environments but serves to trigger processes in the model approach followed here. Under increasing dissolution, the fluid takes up Ca and the Mg/Ca ratio approaches values more typical of natural diagenetic fluids.

The sample exposed to meteoric fluids displayed a significant degree of neomorphism, with the dissolution of the aragonitic framework, and precipitation of large isometric (sometimes rhombohedral) calcite crystals throughout the skeleton (Figures 4G and 5B). The SEM images further documented blocky crystals within the framework and neomorphic textures (Figure 4H). Analyses confirmed the mineralogical transformation from aragonite (<1%) to calcite (>99%) (Table 1; Figures 3 and 5A). In contrast, the burial fluid did not trigger neomorphism to blocky calcite, but instead resulted in minor amounts of dissolution of the primary skeletal framework, and reprecipitation of needle-like aragonite crystals infilling the primary pore space (Figure 4M). These observations were further evidenced by SEM images (Figure 4N) and mineralogy data (Figures 2 and 5B), which confirmed a composition of >99% aragonite.

The significant diagenetic contrast observed can be explained by several factors, including: fluid chemistry (in particular the Mg/Ca ratio, with Mg-rich “burial” and Mg-lean “meteoric” fluids), reaction rates, mineral solubility (Morse et al., 2007), saturation state (Morse & Mackenzie, 1993), mass transport of dissolved carbonate, and diffusive transport mechanisms (Morse et al., 2007; Jonas et al., 2017). In addition to relatively high temperatures, the high fluid-to-solid ratio used
in the experiments (relative to natural environments) would likely result in relatively fast reaction rates once thermodynamic barriers were surpassed (Ritter et al., 2017). Perhaps most importantly, experimental work has documented that the Mg/Ca ratio of the fluid has a significant impact on the nucleation kinetics of different carbonate minerals (Kitano, 1962; Purgstaller, Mavromatis, Immenhauser, & Dietzel, 2016, Purgstaller, Mavromatis, Konrad, & Dietzel 2016). It is emphasized that the experimental conditions used here are not intended to mirror natural systems, but to induce alteration sequences within the sample. Therefore, solutions initially highly undersaturated with respect to aragonite, as well as extremely high Mg/Ca ratios of 250:1 that are both atypical for known natural systems, were used. The incorporation of Mg during volume-to-volume dissolution−reprecipitation of aragonite crystals is unlikely due to the change in coordination from 6 to 9 that is required for the replacement of Ca and hence, aragonite nuclei are more likely to reach a critical surface area-to-volume ratio required to form secondary crystals (Bischoff & Fyfe, 1968; Perdikouri, Kasiotpas, Geisler, Schmidt, & Putnis, 2011, Perdikouri, Piazolo, Kasiotpas, Schmidt, & Putnis, 2013). This may account for the relatively low amounts of Mg within the recrystallized primary portions of the coral skeleton altered in the burial fluid (Figure 6N). Additionally, almost no Mg is incorporated in inorganically formed aragonite.

In contrast, the meteoric diagenetic fluid which contained a higher Na concentration but no Mg resulted in thermodynamic instability of the aragonite skeleton, causing mineralogical replacement of the whole coral skeleton to calcite. Within both systems, the undersaturated diagenetic fluid with respect to aragonite provoked dissolution of the coral skeleton and the initial degradation of organics. However, data shown here document a faster elemental exchange between the fluid and coral in the meteoric sample due to the replacement of aragonite by calcite within porous materials (Jonas et al., 2017). The sample altered in burial fluid was likely replaced as micro-scale dissolution−precipitation of the primary coral framework along a thin veneer reaction front. The replacement rate is generally controlled by the diffusive transport through both the fluid network initially present within the material, and the secondary porosity formed during replacement (Jonas et al., 2017).

Following the initial dissolution and reprecipitation, enough Ca\textsuperscript{2+} ions must have remained within the fluids to result in a second phase of crystallization. Precipitation of pore-filling fibrous aragonite needles in the burial experiments resulted effectively reducing primary porosity, and minimized the formation of secondary porosity. A dissolution−reprecipitation process which did not occur in a volume-by-volume mechanism therefore resulted in the variation in elemental distribution. The inorganic pore-filling aragonite contains relatively higher Mg and Sr, and lower S compared to the primary skeleton (Figure 6M through O). The use of Sr/Ca and primarily Mg/Ca ratios as palaeothermometers (Hart & Cohen, 1996; Shen et al., 1996; Rosenthal & Lohmann, 2002; Barker, Greaves, & Elderfield, 2003; Elderfield, Yu, Anand, Kiefer, & Nyland, 2006) expresses changes in Sr/Ca ratios generally increase in the coral structure (Alibert & McCulloch, 1997). Furthermore, through the study of both experimental and natural coral samples, Smith, Buddemeier, Redalje, & Houck, (1979) showed that Sr/Ca ratios and water temperature have a direct and linear relationship, but also noted a difference in biogenic and inorganic aragonite. Although both temperature-dependent, inorganic aragonite generally has higher distribution coefficients than aragonitic corals that would incorporate less Sr in their crystal structure. This confirms the observations within the experimental sample altered in burial fluids, where secondary needle-like cements are precipitated with comparatively higher amounts of Sr (Figure 6O).

Elemental and organic matter distribution data provide further support for the previously discussed interpretation. Compared to the primary coral skeleton, the secondary needle-like cements of the sample exposed to burial fluids at a temperature of 160°C had relatively high amounts of both Mg and Sr, and low amounts of S (Figure 6M through O). Because the initial experimental burial fluid did not contain any Sr, one can conclude that the Sr incorporated in the cement phase was obtained from the primary skeleton via dissolution as discussed in the previous section. However, dissolution (and initial reprecipitation) must have taken place on a small-scale where ion exchange in the crystal lattice occurred without major mineralogical or textural alteration. Additionally, the initially formed secondary aragonite precipitate may only cover a few layers of the pre-existing aragonite, leaving textural features invisible due to analytical limitations. Nevertheless, similar patterns have previously been reported and commonly linked to diffusion-related processes (Allison, Finch, Newville, & Sutton, 2005; Watson & Müller, 2009). The high Mg/Ca ratios used in the burial fluid experiments created not only initial dissolution, but also inhibited calcite nucleation and growth, while favouring the precipitation of aragonite—a commonly observed feature in both laboratory and natural systems (Purgstaller, Mavromatis, Immenhauser, & Dietzel, 2016 Mavromatis, Konrad, & Dietzel 2016; Purgstaller, Dietzel, Baldermann, & Mavromatis, 2017, Purgstaller, Konrad, Dietzel, Immenhauser, & Mavromatis2017; Konrad et al., 2018). In contrast, the extensively altered meteoric sample contains relatively lower amounts of Mg and higher amounts of Sr in the neomorphosed primary framework, with relatively higher Mg and lower Sr content in the grain bridges (Figure 6H and I). This may indicate that the original aragonite skeleton was first neomorphosed to the blocky calcite textures, leaving relatively lower amounts of Sr to be incorporated in the crystal lattice of the bridging cements.
A general removal of organic matter at the margins resulted in relatively higher concentrations towards the centres of the primary coral framework, whereas diagenetic cement phases were relatively devoid in organics in both fluid types. The relatively higher amounts of dark brown accumulations (Figure 4G and M), and brighter fluorescence (Figure 4I and O) observed towards the centre of the primary framework, indicate the presence of altered organic compounds (Martell, Motekaitis, Fried, Wilson, & MacMillan, 1975). These results suggest that with increasing temperature, organic matter was further degraded compared to the 130°C samples. Particularly in the sample altered in burial fluid, these patterns are enhanced due to the newly formed organic-lean cements which line the initial pore space. Elemental S maps also displayed a relatively higher concentration within the coral framework compared to the diagenetic cements at the higher temperature (Figure 6G and M). Contrary to the pristine sample, which was slightly enriched towards the centre, the altered samples indicate the removal of organics from the outer grain fringes which had the most interaction with the pore fluids, leaving a relatively enriched centre.

4.3 | Isotopic equilibration

Although carbon and oxygen isotope analyses based on samples obtained by micromilling devices (similar to those used in this study) have been shown to slightly alter the δ18O values of some carbonate material due to the transformation of aragonite induced by heat generated in the milling process (Waite & Swart, 2015), the speed with which the samples were drilled here (50 g) was below the threshold at which a change would be expected to occur (Staudigel & Swart, 2016). The two isotope systems analysed here can be controlled by both depositional and diagenetic processes. Generally, δ13C values of a primary coral skeleton are controlled by the: (a) δ13C values of ambient dissolved inorganic carbonate (DIC) in the formation fluid; (b) fluid pH; (c) rate of precipitation (kinetics); (d) mineralogy; and (e) temperature (Swart, 2015). Biogenic δ13C values of the pristine sample range from −1.3 to −2.5‰, with slightly more positive values towards the centre of the sample (Figure 8A), which can likely be attributed to seasonal differences (Swart, 1983; Kuhnert et al., 1999). In these experiments, δ13C values remained generally unchanged regardless of temperature or fluid type (Table 1; Figure 7), with a range of 3‰ for all values (−2.5 to 0.5‰). This low variation is likely due to the “carbonate buffered” conditions created, in which the only carbon pool available was that of the coral aragonite itself, and any carbon incorporated in diagenetic replacement minerals would have derived from the initial aragonite phase. The relatively stable values are to be expected, as the δ13C values of altered carbonate material will only change when a carbon source with significantly different δ13C values is added to the system (Fairbanks & Dodge, 1979; Kuhnert et al., 1999). This is because the oxidation potential of pore waters in a diffusive regime is too low to influence the δ13C value of the carbonate. Thus, the small variation observed in δ13C values between samples is more likely a reflection of the marine fluids at the point coral aragonite is secreted rather than diagenesis. However, slightly lighter isotopic values may have also been caused by organic decay.

In contrast, as oxygen is invariably present in both the carbonate skeleton and the experimental 18O-depleted fluids, any carbonate dissolution, and subsequent re-equilibration with the fluid (or partial equilibration) and reprecipitation should be observed through the isotope analyses. During aragonitic coral growth, δ18O values of corals are influenced by the: (a) temperature of formation fluids; (b) δ18O of the precipitating fluid; (c) mineralogy; (d) fluid pH; as well as (e) non-equilibrium processes considering the DIC and H2O distribution and fluid-solid interface (Swart, 2015). Because all of the samples examined here were taken from one specimen, and the pristine sample had a comparatively limited range (±0.4‰) in δ18O values, we can assume that any major variation in δ18O composition is due to fluid–solid interactions from the alteration experiments. Both samples exposed to the reactive fluids at 160°C showed 18O-depleted values, especially towards the margin and middle portions of the skeleton (Figure 7C and 7), suggesting significant incorporation of fluid-derived oxygen (Duan & Li, 2008; Jonas et al., 2017). This implies that the more 18O-depleted portions are closer to isotopic equilibrium (Coplen, 2007; Watkins, Nielsen, Ryerson, & DePaolo, 2013) with the experimental fluids, which would theoretically be reached if the experiments continued within a closed system and if the experiments have a low precipitation rate.

Due to the low δ18O value of the experimental fluids compared to seawater [−47 versus 0‰ (VSMOW)], exchange of oxygen between the fluid and the Porites sp. coral was easily traced by tracking any substantial deviations from the pristine sample, which averaged −4.2 ± 0.04‰ (Table 1; Figure 8A). The samples exposed to the meteoric fluid revealed a relatively high fluid-to-solid interaction, in agreement with the petrographic diagenetic features. The meteoric samples have average δ18O values of −7.2 ± 0.08 and −49.0 ± 0.16‰ for the 130 and 160°C experiments (Figure 7B,7), respectively. The more 18O-depleted values indicate the aragonite-to-calcite transformation by dissolution–reprecipitation processes. Conversely, the samples altered with burial fluid did not show as significant a change in δ18O values, with averages of −6.8 ± 0.08 and −6.6 ± 0.07‰ for the 130 and 160°C experiments (Figure 7D,7), respectively. These results are also in good agreement with petrographic observations, indicating a lack of mineralogical alteration.

The SIMS isotope analyses provided more precise measurements of individual grains along the lower portions of the Porites sp. samples exposed to experimental temperatures of 160°C. Within the meteoric sample, although the near-complete dissolution of aragonite and reprecipitation of calcite was...
observed, a much larger range of $\delta^{18}O$ values was seen in the SIMS measurements. Ranging from $-3.5$ to $-66.1$‰ (average of $-40.5$‰, $n = 37$) (Figure 8A), some portions of the skeleton indicate retention of near-depositional values. Although only four points were more positive than $-10.0$‰, the large variation of values suggests that the isotopic resetting may take place in a complex manner, and with great spatial variability. Possibly an initial phase of either aragonite-aragonite recrystallization, or aragonite-to-calcite neomorphism, and a later-stage recrystallization closer to isotopic equilibrium took place. With less variation in $\delta^{18}O$ values (ranging from $-5.0$ to $-18.9$‰; average of $-13.2$‰, $n = 23$), most points from the sample exposed to burial fluid indicate an initial resetting, but with a mixture of oxygen from the original skeleton, and from carbonate precipitation from the experimental fluids. However, with a spot size of ca. 15 µm, the former interpretation is most likely. These results imply that isotopic analyses on bulk compositions, such as those previously discussed, are indeed a useful method to investigate $\delta^{18}O$, but that SIMS analyses offer additional insight that may otherwise be overlooked.

### 4.4 Implications for coral research

The experiments performed in this study resulted in a number of petrographic and geochemical features shared with naturally altered samples. Nevertheless, a simple translation of observations made here to the far more complex diagenetic pathways of natural systems is not encouraged. Furthermore, many studies using *Porites* sp. corals for paleoclimatology rarely deal with material buried in conditions which our experiments aim to simulate. From a climate archive perspective, coral skeletons that have seen pervasive neomorphism and replacement by blocky calcites hardly qualify as suitable material, as demonstrated in previous studies (Longman, 1980; Melim, Swart, & Maliva, 1995; Strasser & Strohmenger, 1997). However, a series of important observations can be made from these results that have significance for those working with fossil coral archive material. The aragonite–aragonite diagenesis in the presence of Mg-bearing reactive fluids is one such point, where the predominance of both primary and secondary aragonite might suggest that PXRD analyses of these corals would fail to detect the patterns of alteration (Fernandez-Diaz, Mazur, Gothmann, & Stolarski, 1996; Hendy et al., 2007; McGregor & Abram, 2008; Frankowiak et al., 2013; Krayesky-Self, Richards, Rahmatian, & Fredericq, 2016; Jonas, Richards, Rahmatian, & Fredericq, 2017). The textures observed in these experiments generally mimic naturally altered samples. Within the meteoric sample, the blocky calcite textures (Figure 9A) are similar to those observed in an early Pleistocene (likely) *Porites* sp. coral from Isla Colon, Panama (McNeill et al., 2013) (Figure 9B). Although less studied than the extensive literature on calcite replacement, early diagenetic aragonite cements have been documented as early as the 1970s by Ginsburg & James (1976) and more recently by others (McGregor & Abram, 2008; Frankowiak et al., 2013; Sadler, Webb, Nothdurft, & Dechnik, 2014), and share important characteristics with the results shown here (Figure 9C,9). Pore-filling aragonite needle cements have been reported in Triassic corals from Turkey by Frankowiak et al. (2013) (Figure 9D), which were
predicted to have formed during early stage diagenesis that included the decay of intraskeletal organic matter, and the formation of the secondary cements along the coral walls.

Another important issue is the remarkable resilience of the carbon isotope signatures under rather extreme (high temperatures) diagenetic conditions. Results shown here document that under rock-buffered conditions, carbon isotope signatures of even overprinted aragonites might be of some significance for palaeoenvironmental research. Furthermore, the variation of ion exchange (here, through dissolution–reprecipitation reactions) rate and alteration potential is important for the understanding of diagenesis in different burial conditions. Although different alteration products were observed between the two systems, a general diagenetic progression tends to move from the more labile organic constituents, to the more stable inorganic components within the skeleton. Whether organic structures and patterns partially control the diagenetic process, or if it is simply based on distribution within the altered material may be a topic for further study.

5  |  CONCLUSIONS

This research indicates a complex relationship between petrographic and geochemical responses of the aragonitic coral _Porites_ sp. to different diagenetic conditions. The chosen experimental approach used artificial fluids and significantly elevated temperatures to induce alteration over the experimental interval (4 or 8 weeks). While both fluid types resulted in increasing rates of alteration with increasing temperature, the type and degree of diagenesis vary between the two fluids. Overall, the most significant diagenetic response was observed in the sample heated to 160°C in the meteoric reactive fluid, which included the precipitation of blocky calcite throughout the skeleton and within initial pore space, which was relatively high in Mg, and low in Sr and S. This sample also had the most 18O-depleted values, and almost complete (98.3%) mineral transformation from aragonite to calcite. In contrast, the samples altered with burial fluid showed diagenetic features including slight dissolution, and infilling of pore space with diagenetic fibrous aragonite cements which were relatively high in Sr and Mg, but low in S. Relatively higher δ18O values indicate less re-equilibration with the experimental fluids compared to the meteoric sample. These results suggest that significant diagenesis can occur even in the absence of mineralogical change, as the composition of the sample was still >98.9% aragonite. The authors conclude that organic matter distribution is altered early in the diagenetic process and may be the initial diagenetic response, with inorganic stabilization being a slightly later process. Overall, this study suggests that the degree and type of coral aragonite diagenesis is primarily controlled by the chemistry of the diagenetic fluids.

Accordingly, the main conclusions can be highlighted as follows:

1. Preserved aragonitic material, including textural features, does not necessarily mean no change of proxies during alteration. Thus, following the findings of past research (Hathorne, Felis, James, & Thomas, 2011, and others), the simple approach that aragonite indicates preservation of geochemical signals is not necessarily true.

2. High Mg/Ca ratios, such as in seawater inhibits dissolution of aragonite and its transformation to calcite, and can result in the formation of secondary aragonite. Therefore, meteoric impact during diagenesis will in this case strengthen and accelerate the alteration.

3. Secondary alteration of corals can be indicated by aragonite needles in the pore volume, blocky calcite, and the distribution of organic constituents, in particular S.

4. Assessing stable oxygen isotopic re-setting requires oxygen in the whole system to be dominated by the fluid.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available in the Supporting information, and from the corresponding author upon request.

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