High-resolution hyperspectral imaging of diagenesis and clays in fossil coral reef material: a nondestructive tool for improving environmental and climate reconstructions

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Abstract
Hyperspectral imagery (1000–2500 nm) was used to quantitatively map carbonate and clay minerals in fossil reef cores that are relevant to accurately reconstructing past environmental and climatic conditions. Techniques were developed using hyperspectral imagery of fossil reef cores and cores acquired from three different geological settings, and were validated against independent measures of calcite to aragonite ratios. Aragonite, calcite, and dolomite were distinguished using a combination of the wavelength position and asymmetry of the primary carbonate absorption between 2300 and 2350 nm. Areas of core containing small amounts of calcite (>2–5%) were distinguished from aragonite in imagery of two cores, enabling quantitative maps of these minerals to be constructed. Dolomite was found to be the dominant mineral in another core. Trace amounts of the aluminium-rich clay mineral kaolinite were detected, quantified, and mapped in one core using its diagnostic absorption feature near 2200 nm. The amounts of clay detected from hyperspectral imagery were below the limits of detection by standard X-ray diffraction techniques but its presence was confirmed by Fourier Transform Infrared Spectroscopy. Hyperspectral imagery acquired at high spatial resolution simplifies vetting procedures for secondary carbonate minerals in coral reef cores, significantly reduces sampling time and costs, and is a powerful nondestructive tool to identify well-preserved coral aragonite in cores for uses in paleoclimate, paleoenvironment and paleoecosystem reconstruction.

1. Introduction
Fossil corals and reef systems are key archives of past climatic and environmental change. The carbonate skeletons of corals and other reef biocalcifiers can be precisely dated by Uranium-Thorium and radiocarbon techniques, and provide critical information on, for example, past sea level (including the rate and magnitude of change) and ice-sheet dynamics [e.g., Bard et al., 1990; Chen et al., 1991; Dutton et al., 2015; Leonard et al., 2013; Stirling et al., 1998; Yokoyama et al., 2011], reef ecosystem response to changing environmental conditions [Braithwaite et al., 2004; Webster and Davies, 2003; Webster et al., 2008], including their growth responses to abrupt climatic change [e.g., Dechnik et al., 2015; Harvey and Hopley, 1981; Marshall and Davies, 1982, 1984], and changing depositional environments such as the influx of terrigenous materials [Dunbar and Dickens, 2003; Dunbar et al., 2000; Harper et al., 2015; Page et al., 2003]. Furthermore, coral skeletal trace element and oxygen isotope records have expanded our understanding of globally important interannual climate drivers such as El Niño-Southern Oscillation [Cobb et al., 2013; Cole et al., 1993; Tudhope et al., 2001], North Atlantic Oscillation [Felix et al., 2004], Indian Ocean Dipole [Abram et al., 2007]; changes in ocean circulation [Gagan et al., 1998; Hendy et al., 2002]; and timing and role of the surface ocean in mediating the response of global climate to natural and anthropogenic forcing [Abram et al., 2016; McGregor et al., 2015; Tierney et al., 2015].
Key to the accuracy of past environmental and climate reconstructions is that the fossil reef material is free of diagenesis. During diagenetic transformations, there are exchanges and removal of isotopes and trace elements that change the geochemistry of the original coralline matrix, and in the process degrade, and in some cases destroy, the climatic and environmental signals. Diagenetic changes include meteoric transformation of skeletal aragonite to calcite, common in subaerially exposed Pleistocene or Holocene coral and reef cores; infilling of pore spaces with calcite cement, high-Mg calcite, secondary aragonite, and/or microbialites [e.g., Allison et al., 2007; Hendy et al., 2007; Müller et al., 2004; Sayani et al., 2011]; and cavity filling mud. Diagenetic transformations also occur in living reef corals [Dechnik et al., 2017; Marshall, 1983; McGregor and Abram, 2008; Nothdurft et al., 2007; Sayani et al., 2011; Tucker, 1991]. The spatial distribution of diagenetic products within samples is highly heterogeneous and can occur at the submillimeter scale such that even small amounts of diagenesis can introduce significant errors into estimates [McGregor and Gagan, 2003].

Detecting and avoiding diagenetic alteration in coral reef samples is of utmost importance to paleoclimate research. Rigorous prescreening of samples using petrographic thin section, X-ray diffraction (XRD) or Scanning Electron Microscopy (SEM) is commonly required to exclude samples that contain diagenetic minerals [Hibbert et al., 2016; McGregor and Abram, 2008; Nothdurft and Webb, 2009]. Many studies, for example, exclude samples that have amounts of calcite >2–5% [e.g., Al-Rousan et al., 2007; Muhs et al., 2011, 2012], but studies involving paleoclimate reconstructions commonly exclude samples with >1% calcite [e.g., Felis et al., 2014; McGregor et al., 2013]. These screening methods are expensive, laborious and, because they may be destructive, samples that are used for dating may represent areas adjacent to those used for prescreening, requiring assumptions to be made about the homogeneity of the core at each sample location. Given the spatially heterogeneous nature of diagenic changes in samples, such assumptions may not be valid. Dolomitization is a worst case scenario for preservation of original coral geochemistry and dolomitized corals are invariably avoided for dating [Strasser et al., 1992].

In recent years, data from hyperspectral imaging sensors acquired in the laboratory have been used to identify and quantify minerals and aspects of their geochemistry in rock samples, nondestructively at submillimeter spatial resolutions [Kruse et al., 2011; Murphy et al., 2016; Schneider et al., 2014]. Each pixel in the hyperspectral image records reflected light in numerous spectral bands and at a spectral resolution (~6–10 nm, Full Width Half Maximum) that is sufficient to resolve mineral absorption features. Many minerals, including phyllosilicates and carbonates, have absorption features between 2000 and 2500 nm [Clark, 1999; Hunt and Salisbury, 1970, 1971]. The wavelength position and shape of absorption features are diagnostic for certain minerals and are indicative of aspects of their geochemistry [Bishop et al., 2008; Clark, 1999; Murphy et al., 2014; Mustard and Sunshine, 1999].

Hyperspectral images of fossil reef cores have the potential to provide important information about their mineralogy and geochemistry in relation to two key aspects. First, hyperspectral imaging can identify fossil corals, or parts thereof, that are suitable for sampling for geochemical data (e.g., to provide estimates of age or environmental parameters) by distinguishing and mapping aragonite, calcite, or dolomite. Studies using hyperspectral imagery to quantify carbonate mineralogy in rock samples have focussed largely on calcite and dolomite or mixtures thereof [e.g., Zaini et al., 2014] or diagenetic alteration occurring at much larger spatial scales [e.g., Kurz et al., 2012]. To the best of our knowledge, no previous studies have attempted to distinguish aragonite from either calcite or dolomite in fossil reef cores. The ability to quickly and nondestructively identify areas in fossil reef cores suitable for detailed dating and geochemical analysis has the potential to significantly reduce costs and improve accuracy of chronological and paleoclimatological data extracted from these archives.

Second, the ability to detect clay minerals in cores could provide an important window into sedimentary fluxes in fossil reef environments, including the input of terrigenous sediments [e.g., Abbey et al., 2013; Dechnik et al., 2015; Dunbar and Dickens, 2003], and to identify palaeosols associated with unconformities. Detection of clay minerals by visual inspection or from color photographs of reef material is difficult because they are commonly present in very small amounts and are similar in color to carbonate minerals. Amounts of clay in cores may be below the limits of detection using standard XRD, X-ray fluorescence (XRF), or inductively coupled plasma-mass spectrometry (ICP-MS) methods. Detection of clays in samples at small spatial scales from laboratory hyperspectral imagery is well constrained [e.g., Kruse et al., 2011; Schneider et al., 2014; Uezato et al., 2016]. Subtle absorption features associated with many clay minerals,
including aluminium-rich clays, can be detected, even in the presence of other minerals that may dominate the sample [e.g., in stromatolites; Murphy et al., 2016]. However, the detection of trace amounts of clay in the context of carbonate-rich fossil reef cores is yet to be shown.

The overarching objective of this study is to demonstrate how hyperspectral imagery can be used to provide information from fossil reef cores that is relevant to reconstructing past environmental and climatic conditions. Specifically, our results distinguish the carbonate minerals aragonite, calcite, and dolomite, and detect and quantify aluminium clay minerals. Methods are tested and validated using hyperspectral imagery acquired from samples of core from three different settings (Figure 1): (1) PNG fossil Porites coral from Muschu Island, Papua New Guinea [McGregor and Gagan, 2003]; (2) Dolomitized fossil coral core from Nauru in the western central Pacific Ocean; and (3) Fossil Holocene and Last Interglacial (LIG) reef core from One Tree Reef (OTR) in the southern Great Barrier Reef (GBR). We conclude that hyperspectral imagery is a fast and effective way to identify carbonate minerals in fossil coral reef material.

2. Theoretical Considerations

Hyperspectral imaging sensors measure the amount of light reflected back from a material in numerous, narrow, and contiguous band-passes (ranges of wavelengths). The shape of a reflectance spectrum is controlled by specific absorptions that are diagnostic for a given mineral (e.g., calcite, kaolinite), superimposed onto a spectral background or continuum [Clark et al., 1990]. The shape and brightness of the continuum depends on several factors including broad nonspecific absorptions caused by organic matter or wavelength-dependent scattering effects that are controlled, in part, by the grain size of minerals in the sample. Removal of the spectral background is therefore essential before information from specific absorptions can be extracted [Clark and Roush, 1984].
Carbonate minerals have distinctive absorptions in the shortwave infrared (SWIR) spectrum between 1800 and 2500 nm [Clark et al., 1990; Gaffey, 1986, 1987; Hunt and Salisbury, 1971]. The primary (i.e., most intense) carbonate absorption, caused by vibration of the carbonate (CO$_3^{2-}$) ion, occurs between 2300 and 2350 nm; however, its exact wavelength position depends on the specific composition of the mineral. In calcite (CaCO$_3$), the wavelength of this absorption feature is located at ~2333–2345 nm [Zaini et al., 2014 and references therein]. In dolomite (CaMg(CO$_3$)$_2$), increasing amounts of magnesium cause the wavelength position of the carbonate feature to shift progressively to shorter wavelengths, typically between ~2320 and 2328 nm [Gaffey, 1987; Pontual et al., 1997]. Zaini et al. [2014] found that the wavelength position of the primary carbonate feature is a reliable indicator of magnesium present in the carbonate, and thus, can be used to distinguish calcite from dolomite. This feature in both calcite and dolomite is markedly left-asymmetric about its absorption maximum, i.e., the area on the shortwave (left) side is greater than the area on the longwave (right) side of the feature. A less intense secondary carbonate feature is located toward shorter wavelengths, between 2156 and 2160 nm or at 2140 nm in calcite and dolomite, respectively [Pontual et al., 1997]. Aragonite in coral and other skeletal carbonates has a less intense, primary carbonate absorption between 2300 and 2350 nm [Gaffey, 1985, 1988]. In aragonite, the secondary carbonate feature observed in calcite and dolomite is not present. This seems to be a consistent attribute of aragonite (see also spectra presented by Craig et al. [2009] and Smyth et al. [2014]). Alteration of aragonite to calcite causes a deepening of the primary carbonate absorption feature, an increase in its left-asymmetry, and the appearance of the secondary carbonate feature between 2140 and 2160 nm [Gaffey, 1985]. A broad range of aluminum-rich clay minerals, including kaolinite and montmorillonite, have sharp, diagnostic absorptions near 2200 nm [Bishop et al., 2008; Clark, 1999; Hunt and Ashley, 1979]. These clay absorption features are detectable even in spectra that have intense carbonate absorption features [e.g., Crowley, 1986].

The wavelength position and the shape of an absorption feature convey important information about mineral type and chemistry. Absorption feature shape can be described by its width and asymmetry [Mustard and Sunshine, 1999]. Absorption feature intensity is an indicator of mineral abundance [Clark et al., 1990, 1991]. Together, these feature parameters could be used as a basis for distinguishing aragonite, calcite, and dolomite, and quantifying the abundance of clay minerals.

### 3. Materials and Methods

#### 3.1. Core Samples

**3.1.1. PNG Fossil Porites Coral**

Fossil *Porites* sp. coral FM19 was used previously to investigate geochemical and petrographic changes to coral aragonite due to diagenesis [McGregor and Gagan, 2003; McGregor and Abram, 2008]. As such, the coral provides a target for comparison to the hyperspectral results. Coral FM19 is part of an uplifted reef that ranges in age from 1360 to 1870 yr BP [McGregor and Gagan, 2003]. The coral stands as an isolated coral head ~2 m high and ~1.5 m in diameter, almost completely exposed in the intertidal zone in Reibiew Bay, Muschu Island (03°25’S 143°35’E), PNG. Diagenesis of coral FM19 occurred in this meteoric vadose environment. A 1.1 m core was drilled from FM19 in 1998 as part of Leg 6b of Project TROPICS (Tropical River-Ocean Processes In Coastal Settings); about halfway down this core the coral aragonite alters to calcite. Petrographic, geochemical, and XRD analysis of FM19 were made along a 7 mm slice taken along the major growth axis of the core. The analyses showed distinctive textural changes and a decrease in Sr/Ca and δ$^{18}$O as the percent calcite increased to 100% calcite (details in McGregor and Gagan [2003]; McGregor and Abram [2008]). In summary, the vadose zone diagenetic sequence observed in coral FM19 began with leaching of primary aragonite (3–5% calcite) and fine calcite overgrowths, transitional to calcite void filling (10–30% calcite), and neomorphic, fabric selective replacement, where the coral skeleton aragonite is replaced with calcite without destroying the gross coral morphology (40–60% calcite). At 75–100% calcite, the aragonite skeleton is completely replaced, coral skeletal elements are present as “ghosts” of the original texture, and single crystal calcite spar fills the voids. The sensitivity of coral Sr/Ca to vadose-zone calcite diagenesis is equivalent to a sea surface temperature (SST) increase of 1.1 to 1.5°C per percent calcite (based on the average calibration of coral Sr/Ca to SST). Coral δ$^{18}$O is less sensitive, with the rate of change in coral δ$^{18}$O-SST at ~0.2 to 0.2°C per percent calcite.
3.1.2. Dolomitized Coral Core

Nauru is a karstified dolomitic limestone island capping a volcanic seamount that rises 4300 m from the seafloor of the Pacific Ocean (0°32’S, 166°56’E). Fossil coral cores were collected from exposed fossil reefs on the central plateau of the island and on isolated coral heads on the Anibare Reef terrace. The sample is most likely Quaternary in age, but this has not been confirmed absolutely because diagenetic alteration precludes radiometric dating of the samples. Nauru hosts a complex diagenetic history dating back to the early stages of uplift in the mid to late Cretaceous (Hill and Jacobson, 1989).

3.1.3. One Tree Reef Holocene and Last Interglacial (OTR Holocene-LIG) Core

OTR is part of the Capricorn-Bunker groups of reefs in the Southern GBR. The windward and leeward margins of OTR are raised and surround a lagoon. For further information on the depositional setting, see Barrett and Webster (2012) and Dechnik et al. (2015).

Core 13 (23°30’S, 152°5’E) used in this study was collected from a patch reef in the OTR lagoon in September 2015. The core penetrated 29 m below the modern reef surface, and includes the entire Holocene and LIG fossil reef sequences. Detailed petrologic and geochemical analysis of other OTR cores by Dechnik et al. [2017] confirmed that the LIG reef sequences were exposed to meteoric diagenesis, including dissolution, recrystallization, and precipitation of blocky calcite cements. The samples used in this study were selected from across the Holocene and LIG boundary in Core 13.

3.2. Hyperspectral Data: Acquisition and Preprocessing

Hyperspectral images were acquired by a shortwave infrared (SWIR; 1000–2500 nm) sensor (Specim, Oulu, Finland). The sensor was mounted on a metal frame, pointing downward onto a linear scanning table onto which the samples were placed. Prior to imagery being acquired from the samples, data (~1000 frames) were recorded from a reflectance standard (~99% Spectralon). The mean distance between the sensor objective and the samples was 250 mm, resulting in each square image pixel being ~0.33 mm. Two arrays of seven halogen lights each illuminated the samples from opposite directions on the scanning table. The integration time of the sensors was adjusted so that no pixels were saturated, i.e., they did not attain the maximal value represented by the bit-depth of the sensor (14 bits). Data were corrected for dark current and calibrated to reflectance on a line-by-line basis. Reflectance was derived by dividing data from each across-track line by the data from the corresponding line from the calibration panel, thereby removing small variations in incident illumination across the samples. Absolute reflectance was derived by multiplying the resulting quotient by the panel calibration factor for each spectral band.

3.3. Quantifying Feature Parameters Using Automated Feature Extraction (AFE)

AFE was used to automatically identify the most intense absorption within a specified wavelength range and quantify its wavelength position, intensity, width at half maximum intensity, and asymmetry [Kruse, 1988; Murphy, 1995]. An advantage of AFE is that subtle changes in the wavelength position and shape of the absorption feature can be quantified, enabling small changes in mineralogy to be detected [Zaini et al., 2014].

3.3.1. General Method

AFE assumes that the spectral continuum has been removed from each spectrum. The continuum for each spectrum in the image was defined empirically by fitting a series of straight line segments across the high-points in the spectrum (shown using kaolinite and calcite as examples in Figure 2a). The continuum is removed by dividing the reflectance of the spectrum by the reflectance of the continuum at each wavelength in the spectrum [Clark and Roush, 1984]. The resulting spectra, henceforth termed normalized spectra (Figure 2b), place all absorptions onto the same reference plane (unity, indicating no absorption). In normalized spectra, increasing amounts of absorption are indicated by decreasing values of normalized reflectance. Feature parameters (wavelength position, intensity, width, and asymmetry) are then determined (Figure 2c). First, the wavelengths of the maximal absorption in the spectrum ($\lambda_{\text{max}}$) and the adjacent wavelengths ($\lambda_{\text{min}} - 1$, $\lambda_{\text{min}} + 1$) were determined; from these, the true wavelength of the absorption feature was obtained by quadratic interpolation using the method of Rodger et al. [2012]. The intensity of the feature was calculated as 1 minus the normalized reflectance at the wavelength of maximal absorption (vertical red arrow). Absorption feature width (in nm) was calculated by interpolating the wavelengths on the short and long-wave sides of the feature at exactly half its maximal intensity. Width was calculated as the absolute difference between these wavelengths (horizontal red arrow). Asymmetry was determined by first
calculating the area on the left and right halves of the feature by integrating the 1 minus normalized reflectance values between the wavelength of the feature minimum to the short-wave (SWL) and long-wave (LWL) limits of the feature, respectively. Asymmetry is then calculated by taking the log of the right area divided by the left area. This scales the resulting values so that a value of zero indicates no asymmetry (i.e., the feature is symmetric) and increasing positive and negative values indicate, respectively, increasing right and left-asymmetry. An image describing the feature parameters was created where each band in the image represented a separate feature parameter. Pixels where no absorption was found were set to zero.

### 3.3.2. Mapping of Carbonates and Clay Using AFE

Separate AFE analyses were used to parameterize absorption features in two different parts of the spectrum; AFE-1 was applied to the wavelength range 2157–2430 nm and AFE-2 to the wavelength range 2114–2255 nm.

AFE-1 was used to parameterize the primary carbonate absorption in order to distinguish between aragonite, calcite, and dolomite.

AFE-2 was used to parameterize the most intense feature between 2114 and 2255 nm, which could be either the secondary carbonate feature and/or features associated with aluminium-rich (Al-OH) clays (e.g., kaolinite). The parameters from absorptions in this spectral range will be used to:

- distinguish Al-OH clay minerals from calcite or dolomite, and;
- quantify the intensity of Al-OH clay absorption as an index of clay abundance. A map describing the intensity of absorption by Al-OH clay minerals was constructed by considering only those pixels in the image where AFE found an absorption between 2180 and 2228 nm, i.e., the wavelength range where Al-OH clay minerals absorb [Clark et al., 1990; Pontual et al., 1997]. Pixels outside of this wavelength range (i.e., pixels where the secondary carbonate absorption was detected as the deepest feature) or pixels where no absorption was found were set to zero. Identification of the specific clay mineral causing the Al-OH absorption was done by extracting spectra from pixels that were identified by AFE as having Al-OH absorption and comparing them to spectra in the USGS spectral library [Clark et al., 1990, 1993].

### 3.4. Spectral Library of Calcite, Dolomite, and Aragonite

To determine a priori which feature parameters would likely yield the best discriminators of aragonite, calcite, and dolomite, a spectral library representative of each mineral endmember was constructed. Hyperspectral imagery was acquired from separate rock samples known from XRD analyses to be dominantly
Validation of quantitative mineral maps derived from hyperspectral imagery was done by comparing results with those from collocated areas of the core that were sampled for laboratory assay. The PNG fossil *Porites* coral was sampled along a transect across the aragonite-calcite boundary by McGregor and Gagan [2003]. Eleven 7 mm long samples were acquired across the boundary using a dental drill (Figure 1a). The Dolomitized coral core was sampled in rectangular blocks (Figure 1b). Eight, visually distinctive areas of cores were subsampled for XRD analysis. The OTR Holocene-LIG core was analyzed by powder X-ray diffraction at QUT’s Central Analytical Research Facility (CARF). The samples were subsampled based on visually distinctive areas for XRD analysis. The subsamples were cut into ~5 mm chips using a diamond saw. These chips were then manually crushed and powdered using a mortar and pestle, with 96% ethanol. Samples were diluted with corundum (Al$_2$O$_3$), micronized with an agate micronizer (zirconium oxide pellets were added to compose of, respectively, each of these minerals. Whole rocks or core samples were used in preference to powdered samples because they contained variations in surface texture and brightness similar to those observed on the core samples. For the aragonite endmember, library spectra were acquired from a fossil coral and a pristine modern coral. The fossil coral (*Porites* sp.) was from a different section of coral FM19 (see section 3.1); XRD analysis indicated that it is comprised of 0.1% calcite [see Table 1 in McGregor and Abram, 2008, sample number XRDFM19-AR]. The pristine modern coral MS01 (*Porites lutea*), was determined from analysis of thin sections to contain no calcite [McGregor and Abram, 2008].

For most samples, average reflectance values were calculated within 10 randomly positioned regions (each 16 pixels in size) within imagery of each endmember sample. For the fossil *Porites* sp. coral (FM19), regions were positioned adjacent to the specific area sampled for XRD. Spectra of calcite (WS272) and dolomite (HS102.3B) from the USGS spectral library were used for comparison. No spectra of aragonite were available from this library. For consistency, spectra from the USGS library were convolved to the band passes of the imaging sensor used in this study using a Gaussian full-width-half-maximum sensitivity function for each spectral band of the image. Endmember spectra obtained as part of this study and from the USGS spectral library are henceforth referred to as “Library” and “USGS” spectra, respectively. AFE was used to parameterize the primary carbonate feature in all Library and USGS spectra using the wavelength range specified for AFE-1 (2157–2430 nm).

### 3.5. Selecting Feature Parameters for Distinguishing Carbonates

Not all feature parameters derived using AFE may be suitable for distinguishing carbonate minerals. To determine which suite of parameters are optimal for this task, relationships between feature parameters derived from the Library and USGS spectra were examined by plotting separately asymmetry, width, and intensity against wavelength position. Wavelength position was used in all plots because, of all the feature parameters, it is most indicative of mineral type and chemistry. Using these plots, the optimal suite of feature parameters that provided the best separation of carbonate minerals was selected (see Results, section 4.2). A classified map of carbonates could then be constructed by incorporating the selected parameters into a parallelepiped classifier [Richards, 1999], encoding simple decision rules.

### 3.6. Laboratory Assays

Validation of quantitative mineral maps derived from hyperspectral imagery was done by comparing results with those from collocated areas of the core that were sampled for laboratory assay. The PNG fossil *Porites* coral was sampled along a transect across the aragonite-calcite boundary by McGregor and Gagan [2003]. Eleven 7 mm long samples were acquired across the boundary using a dental drill (Figure 1a). The Dolomitized coral core was sampled in rectangular blocks (Figure 1b). Eight, visually distinctive areas of cores were subsampled for XRD analysis. The OTR Holocene-LIG core was sampled using the results from the hyperspectral analysis of carbonate type together with a map of compositional types as a guide to ensure that different carbonates (aragonite, calcite) and material types were included. Seventeen samples in total were acquired from areas mapped as calcite or aragonite across different compositional types (coral, altered coral, coralline algae, microbialite, grainstone/packstone; Figure 1c).

#### 3.6.1. X-Ray Diffraction

Samples from the PNG fossil *Porites* coral were pulverized under ethanol and analyzed using a Sietronics Diffractometer with Cobalt radiation [details in McGregor and Gagan, 2003]. Diffraction peaks were analyzed with SIRQUANT v. 2.5 software and using the Rietveld method, with an uncertainty of ±2%.

The OTR Holocene-LIG core and the dolomitized coral core were analyzed by powder X-ray diffraction at QUT’s Central Analytical Research Facility (CARF). The samples were subsampled based on visually distinctive areas for XRD analysis. The subsamples were cut into ~5 mm chips using a diamond saw. These chips were then manually crushed and powdered using a mortar and pestle, with 96% ethanol. Samples were diluted with corundum (Al$_2$O$_3$), micronized with an agate micronizer (zirconium oxide pellets were added to

### Table 1. Decision Rules Used to Classify Carbonate Minerals Using Feature Parameters Wavelength Position and Asymmetry

<table>
<thead>
<tr>
<th>Carbonate</th>
<th>Wavelength Position</th>
<th>Asymmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>≥ 2333 nm and ≤ 2340 nm</td>
<td>&lt;−0.35</td>
</tr>
<tr>
<td>Dolomite</td>
<td>≥ 2312 nm and ≤ 2323 nm</td>
<td>&lt;−0.35</td>
</tr>
<tr>
<td>Aragonite</td>
<td>≥ 2308 nm and ≤ 2322 nm</td>
<td>&lt;−0.35</td>
</tr>
</tbody>
</table>

* A pixel is classified as a particular class only if both feature parameters conform to the decision rules for that class (calcite, dolomite, or aragonite).
dolomitized samples) to a powder (≤10 μm), and then pressed into pellets for XRD analysis. Measurement of diffraction was made using a Bruker DF Endeavor XRD with Cobalt radiation. Crystalline materials were identified using Bruker “Diffracplus EVA” Search/Match software and the ICDD PDF-2 database. For mixed materials, mineral detection limit is usually around 2%. Some minerals although not reported, may be present in amounts < 2%. Quantities were estimated using TOPAS analytical software.

3.6.2. Fourier Transform Infrared (FT-NIR) Spectroscopy

NIR spectra were recorded on a Nicolet Nexus Fourier Transform Infrared (FT-IR) spectrometer (Thermo Fisher PL, Madison, WI, USA) using a Nicolet Near IR Fiber Port optic probe, optimized with a quartz beam splitter, an InGaAs detector, and a NIR source. Spectra were obtained by pointing the probe at suspected clay-rich and clay poor regions of the core (Sample # 5, 7, 8; Figure 1c) and to a powdered kaolinite standard.

4. Results

4.1. Spectral Characteristics of Calcite, Dolomite, and Aragonite

Reflectance spectra of calcite and dolomite exhibit an intense, relatively broad and left-asymmetric carbonate absorption feature at about 2338 nm and 2319 nm, respectively (Figures 3a and 3b). A weaker secondary carbonate feature is present toward shorter wavelengths in calcite (2156 nm) and dolomite (2140 nm).

![Spectral characteristics (2000–2500 nm) of calcite, dolomite, and aragonite. Reflectance spectra are from known rock samples (Library spectra; black line) and the USGS spectral library (USGS spectra; blue line). No USGS spectra were available for aragonite; library spectra of fossil (Porites sp.) and modern (Porites lutea) corals were therefore used as endmembers.](image)

Figure 3. Spectral characteristics (2000–2500 nm) of calcite, dolomite, and aragonite. Reflectance spectra are from known rock samples (Library spectra; black line) and the USGS spectral library (USGS spectra; blue line). No USGS spectra were available for aragonite; library spectra of fossil (Porites sp.) and modern (Porites lutea) corals were therefore used as endmembers. (top: a–c) Absolute reflectance spectra for calcite, dolomite, and aragonite; (bottom: d–f) the corresponding normalized spectra from which feature parameters are derived. Library spectra from rock/coral samples are averages (n = 10; SD near 2050 nm is indicated in Figures 3a–3c). Wavelength positions of the primary carbonate absorption feature before and after normalization are indicated (cf., wavelength positions in Figures 3a–3c with those in Figures 3d–3f). The left and right halves of the main carbonate absorption used to derive asymmetry are delimited (vertical red dashed line in Figures 3d–3f). The weaker (i.e., secondary) carbonate absorption located at 2156 nm (calcite) and 2140 nm (dolomite) is indicated (red arrow; d and e, respectively). Note that the aragonite spectra do not exhibit this feature (f). The apparent absorption located between 2400 and 2500 nm (gray area) is an artefact from the spectral normalization and is not considered in any analyses. Average parameter values (n = 10) are indicated in Figures 3d–3f.
The average reflectance spectra of fossil Porites sp. and modern Porites lutea coral representing the aragonite endmember have a similar curve shape and exhibit a weak, discrete, and apparently left-asymmetric absorption centered at ~2334 nm (Figure 3c). Unlike calcite or dolomite, the absorption to shorter wavelengths is not present in either spectrum, consistent with published spectra of aragonite [Gaffey, 1988]. Normalized reflectance spectra show the true wavelength position and relative intensities of absorption features in each spectrum (Figured 3d–3f), allowing the feature parameters to be calculated. The effects of normalization on wavelength position and intensity can be seen in all spectra. For example, the intensity of the calcite absorption at 2338–2339 nm appears to be greater than that of dolomite at 2319 nm (Figures 3a and 3b), but following normalization, the opposite relationship is observed with dolomite having the more intense feature (Figures 3d and 3e). As a result of normalization, the wavelength position of the feature present in the average reflectance spectra of aragonite (Porites sp. and Porites lutea; 2334 nm) is shifted to its true positions at 2315 and 2313 nm (cf., Figures 3c and 3f). Normalization also changes the apparent asymmetry of the carbonate feature in the aragonite spectra from left-asymmetric (reflectance; Figure 3c) to relatively symmetric (normalized reflectance; Figure 3f). The apparent absorption at wavelengths greater than 2400 nm is an artefact of the normalization process and is not used in any subsequent analyses (gray area in Figures 3d–3f).

4.2. Optimal Feature Parameters for Distinguishing Carbonates

Aragonite spectra represented by the pristine modern Porites lutea coral all had absorptions with an asymmetry centered on zero (i.e., the absorption was symmetrical), as did 7 out of 10 spectra from the fossil Porites sp. coral (Figure 4a). The wavelength position of the carbonate absorption in these spectra was between 2311 and 2318 nm. Three spectra from the fossil Porites sp. coral had longer wavelengths and increased negative asymmetry, suggesting these spectra were less pure. These data show that aragonite and calcite can be separated using wavelength position alone, as can calcite and dolomite. Separation of dolomite from aragonite is more problematic because the wavelength positions of their primary carbonate absorption feature are similar. The wavelength position and asymmetry of calcite and dolomite in the Library spectra show little variability and are very similar to those in the USGS spectra (Figure 4a). Although aragonite and dolomite could not be distinguished on the basis of wavelength position alone, these minerals can be distinguished using a combination of their wavelength position and asymmetry.

The width of the carbonate absorption feature with respect to wavelength position showed greater variability than did asymmetry, causing some overlap between the Library spectra for calcite and aragonite (cf., Figures 4a and 4b). Differences in the width of the carbonate absorption between, respectively, the Library spectra of calcite and dolomite and the corresponding USGS spectra were greater than were observed for the asymmetry parameter. For these reasons, width was not selected as a suitable feature parameter to discriminate between carbonate minerals. Although intensity could be potentially used to distinguish carbonates (Figure 4c), it can be highly variable because it is a function of mineral abundance. Taken together,
these findings indicate that wavelength position and asymmetry present the best parameters to enable calcite, dolomite, and aragonite to be distinguished and were used to classify carbonates in hyperspectral imagery with a parallelepiped classifier encoding simple decision rules (Table 1). A pixel was classified as calcite, dolomite, or aragonite only if conditions for both wavelength and asymmetry were met. Intensity is used in this study but only as an index of abundance.

4.3. Distinguishing Carbonates Using Feature Parameters of the Primary Carbonate Absorption (AFE-1)

4.3.1. PNG Fossil Porites Coral

True color images of the cut surfaces of the PNG fossil Porites coral are shown in Figure 1a. The aragonite-calcite boundary (dashed black line) separates the predominantly calcite (to the left of the line) and aragonite (to the right of the line) parts of the coral. These different parts of the coral are different in color and texture. Two discrete areas of the sample are highlighted by the feature parameters (Figure 5). The wavelength position of the primary carbonate absorption is distributed between two discrete groups centered on ~2312 and 2335 nm indicative of aragonite and calcite, respectively (Figure 5a). Asymmetry of the carbonate absorption can be broadly assigned into one of two groups centered on ~ -0.1 and ~ -0.5 (Figure 5b). A boundary of intermediate values (~ -0.4) of variable thickness is located between these groups suggesting a transition zone of mixed aragonite and calcite. Within this area, there are large variations in the intensity of the carbonate feature indicating variations in the abundance and/or crystallinity of calcite (Figure 5c). These variations are not evident in the images of wavelength position or asymmetry. The boundary between the calcite and aragonite has the smallest intensity values within the samples, including the area of aragonite.

The classified map of carbonates constructed by combining information on the wavelength position and asymmetry parameters showed that the diagenetically altered area was composed of calcite; the remainder of the sample was composed of aragonite (Figure 5d). The size and shape of the area of calcite in section B, as defined by wavelength position, asymmetry, and the classified map, is consistent with published X-Ray
positive images of this sample [sample FM19; McGregor and Gagan, 2003; Figure 5e]. No pixels were classified as dolomite. Several areas in the image had pixels that were unclassified (i.e., they did not conform to any of the decision rules in Table 1). Unclassified pixels tend to be located along the boundary between the diagenetically altered and unaltered areas of the sample.

To validate the results from the AFE-1 analysis, image values of wavelength position and asymmetry across the aragonite-calcite transect were extracted from the image and compared with results from XRD analyses from McGregor and Gagan [2003]. Pixels were extracted across the full height and length of the transect (see Figure 1a; inset). Average values determined for each column of pixels representing the height of the transect provided a contiguous measure of wavelength position and asymmetry across its entire length. Additionally, average values of wavelength position and asymmetry were calculated from each of the locations along the length of transect sampled for XRD analysis. Large variations in wavelength position and asymmetry were found across the aragonite-calcite boundary (Figure 6a). The smallest wavelengths and the smallest negative values of asymmetry (indicating greater symmetry of the carbonate feature) are located at the start of the transect. Proportions of calcite in this part of the transect are small (<5%). A sharp increase in wavelength position and increasing negative values of asymmetry (indicating increasing left asymmetry of the carbonate feature) occur across the aragonite-calcite boundary, consistent with increasing proportion of calcite in the sample. Proportions of calcite determined by XRD in this part of the transect are much larger (31 – 64%). A sudden decrease in wavelength position and a decrease in negative values of asymmetry indicate a localized decrease in calcite (to 13%). Taken together, these data indicate that wavelength position and asymmetry of the primary carbonate absorption feature enable aragonite to be quantitatively distinguished from calcite in these coral sections.

4.3.2. Dolomitized Coral Core

Scanning all sections of the dolomitized coral core, AFE-1 found only small variations in wavelength position of the primary carbonate absorption feature ranging from \(~2318\) to \(2323\) nm (Figure 7a). Absorptions within this wavelength range are indicative of either aragonite or dolomite. The small variations in wavelength position across the cores suggest that they are compositionally homogenous. Asymmetry was more variable within Section A of the core than other sections (Figure 7b). Intensity was the most variable of all feature parameters (Figure 7c), showing large variations in sections B and C—parts of the core that had shown only small variations in wavelength position and asymmetry.
The classified maps of carbonate type created by combining wavelength position and asymmetry reveal that the sample are almost exclusively composed of dolomite (Figure 7d; Table 2). Between 81 and 100% of pixels within areas of the core sampled for XRD analysis were classified as dolomite. Results from XRD analysis showed that these samples were composed of between 82 and 91% dolomite, thus validating the results from the hyperspectral imagery.

4.3.3. OTR Holocene-LIG Core

A visual classification of a color image of the cores revealed six categories of material: coral, coralline algae, microbialite, grainstone/packstone, altered coral, and unidentified material [Dechnik et al., 2015, 2017]. Images quantifying wavelength position, intensity, and asymmetry of the primary carbonate feature between 2300 and 2350 nm are shown in Figure 8. The wavelength position of the feature ranged from 2308 to 2338 nm, with wavelengths being distributed into two discrete groups centered on 2317 and 2337 nm. Absorptions near 2317 nm are indicative of either aragonite or dolomite and absorptions near 2337 nm are indicative of calcite (Figure 8a; see also Figure 4). Discrete, small areas of pixels with intermediate wavelengths (2325 nm) are also present in some sections of core (e.g., the bottom left of section B and the top right of section C). Asymmetry of the primary carbonate absorption revealed a similar spatial pattern to wavelength position with pixels forming into two discrete groups centered on ~0.01 to ~0.02, indicative of aragonite and ~0.36 to 0.46 indicative of either calcite or dolomite. Small areas of

<table>
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<th>Feature Parameters</th>
<th>Classified Pixels (%)</th>
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*Feature parameters and the percentage of pixels classified as calcite, dolomite, or aragonite are from collocated areas in the image where the samples were acquired. Figures in bold indicate the samples where dolomite has been correctly identified by AFE-1 as being the dominant mineral. Pure quartz was introduced during preparation.

*Nondiffracting or unclassified minerals.

*Percentage of image pixels that were not classified (i.e., they did not conform to any of the decision rules in Table 1).
pixels of intermediate asymmetry (~0.21) were consistent with areas that had an intermediate wavelength position (e.g., the bottom left of section B and the top right of section C; cf. Figures 8a and 8b). The intensity of the primary carbonate feature was very variable, ranging from ~0.03 to 0.40 (Figure 8c) indicating large variations in the abundance and/or crystallinity of carbonate in the core.

A classified map of carbonates showed that calcite and aragonite, but not dolomite, were present in the OTR Holocene-LIG core (Figure 8d). Areas within some sections of core were unclassified. Unclassified areas tended to be along the boundaries between areas of calcite and aragonite or in areas that exhibited intermediate values in either wavelength position or asymmetry (e.g., sections A, B, and C; cf., Figures 8a, 8b, and 8d). To evaluate the classified map of carbonate type, the percentages of pixels classified as either calcite, dolomite, or aragonite in each of the areas sampled for XRD analysis were calculated (Table 3). These data indicate that the classified map of carbonate type was entirely consistent with dominant carbonate mineralogy as determined from XRD (details provided in supporting information S1).
Table 3. Comparison of Results From XRD With Feature Parameters and Carbonate Classification Derived From the Primary Carbonate Absorption Feature (AFE1)

<table>
<thead>
<tr>
<th>Samples</th>
<th>XRD (wt.%)</th>
<th>Feature Parameters</th>
<th>Classified Pixels (%)</th>
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</table>

*XRD data are from samples acquired from the OTR Holocene-LIG core (see also Figure 1c). Feature parameters and the percentage of pixels classified as calcite, dolomite, or aragonite are from collocated areas in the image where the samples were acquired. Figures in bold indicate the samples where aragonite has been correctly identified by AFE-1 as being the dominant mineral (i.e., percentage amounts of calcite were below the upper acceptable threshold (5%). Pure quartz was introduced during preparation.

**Non-diffracting or unclassified minerals;

Percentage of image pixels that were not classified (i.e., they did not conform to any of the decision rules in Table 1).

4.4. Quantitative Relationships Between Feature Parameters and XRD Estimates of Aragonite and Calcite

Quantitative relationships between feature parameters (wavelength position and asymmetry) of the primary carbonate absorption feature and XRD estimates of calcite and aragonite were examined by combining the data from the PNG Porites coral and the OTR Holocene-LIG core (Figure 9). Relationships between wavelength position and amounts of calcite were best described by a logarithmic model with two parameters (R² = 0.90; SE = 2.82; p < 0.0001; Figure 9a). At smaller amounts of calcite (<13%), small increases in amounts of calcite from <5 to 7–13% caused relatively large changes in wavelength position from an average of 2316 nm to an average of 2327 nm. At larger calcite concentrations (> ~30%), wavelength position continued to increase but the slope of change was smaller. The relationship between asymmetry and amounts of calcite is best described by an exponential decay model with three parameters (R² = 0.94; SE = 0.03; p < 0.0001; Figure 9b). Like wavelength position, at smaller amounts of calcite (≤13%), small increases in calcite from <5 to 7–13% caused large increases in negative asymmetry from an average of −0.09 to an average of −0.28. At larger amounts of calcite (> ~30%), no further significant decreases in negative asymmetry were evident with asymmetry remaining at an average of −0.41. Thus, large changes in wavelength position and asymmetry occurred where amounts of calcite were small (≤13%), indicating that these feature parameters are sensitive to changes in amounts of calcite over a range relevant to estimating chronology and paleoclimatological variables from fossil reef cores. Data representing the aragonite endmember from core FM19 were not used in these regressions. However, when those data are plotted on the graphs they are in close agreement with the lines of best fit (cross in Figures 9a–9d).

Relationships between wavelength position or asymmetry and amounts of calcite at amounts ≤13% appeared to be linear. A plot of wavelength position and amounts of calcite ≤13% showed large amounts of scatter among the data points (Figure 9c). It was not therefore appropriate to derive a linear model to describe relationships between these data. A strong linear relationship was found between asymmetry and amounts of calcite (Figure 9d). Data representing the aragonite endmember from core FM19 are in close agreement with the linear fit. These data show that small changes in amount of calcite from 0.1% (core FM19) to 1% (the smallest amount of calcite detected in the OTR Holocene-LIG core) resulted in a change in asymmetry from −0.03 to −0.08. Inverting the linear regression equation showed that amounts of calcite could be predicted from asymmetry to within ± 2%.
4.5. Distinguishing Aluminium-Rich Clay Minerals From Carbonates and Quantifying Their Abundance (AFE-2)

No clay minerals were found in the PNG fossil Porites coral or in the dolomitized coral core by AFE-2 (Figures 10a and 10b). A single absorption was found by AFE-2 in the PNG fossil Porites coral at \( /C24 \approx 2157 \text{ nm} \) (Figure 10a) and in the dolomitized coral core at \( /C24 \approx 2140 \text{ nm} \) (Figure 10b), indicative of secondary absorption by calcite or dolomite, respectively. The size and shape of the area mapped as calcite in the PNG fossil Porites coral by AFE-2 closely matched that of the area mapped as calcite by AFE-1 (cf. Figures 10a and 5). The dolomitized coral core showed consistent absorption across all sections of the core with little variation (Figure 10b).

AFE-2 found two groups of absorptions in the OTR Holocene-LIG core, centered on \( /C24 \approx 2157 \text{ nm} \) and \( /C24 \approx 2207 \text{ nm} \), indicative of calcite and Al-OH clay, respectively (Figure 10c). Pixels with Al-OH clay absorption were patchily distributed and had very small intensities, the most intense of these being located in core sections F, G, and H within the LIG reef sequence (Figure 10d). Large sections of core (e.g., section B) did not exhibit either a carbonate or clay absorption (black areas; Figure 10d).

Reflectance spectra typical of areas in the image that were found to have absorption by Al-OH clay or calcite or that had no absorption were further examined (Figure 11). Typical reflectance spectra from pixels where Al-OH clay absorption was found exhibited a discrete absorption at \( /C24 \approx 2207 \text{ nm} \) (Figure 11a; green symbols). The shape of this feature was consistent with published spectra of limestone (calcite) with kaolinite impurities [Crowley, 1986]. Normalized spectra showed that this Al-OH feature was a doublet with separate

![Figure 9. Relationships between feature parameters and amounts of aragonite and calcite determined by XRD analyses from the PNG fossil Porites sp. coral (FM19; closed circles) made by McGregor and Gagan [2003] and the OTR Holocene-LIG core (open circles; this study): (a) Wavelength position versus amounts of calcite, (b) Asymmetry versus amounts of calcite, (c) Wavelength position versus amounts of calcite \((< 13\%))\), and (d) Asymmetry versus amounts of calcite \((< 13\%))\). In each graph, the pure aragonite endmember from the fossil Porites sp. coral (FM19) is shown (blue cross). Note that this point was not included in any analysis of regression.](image-url)
Figure 10. Feature parameters derived from AFE-2 analysis: (a) Wavelength position (nm) from the PNG *Porites* coral. (b) Wavelength position (nm) from the Dolomitized coral core. (c) Wavelength position (nm) from the OTR Holocene-LIG core. The vertical white line marks the boundary between the Holocene and Pleistocene portions of the core. Labels A to P indicate the sequence of the core sections from the youngest (A) to the oldest (P). Location of samples acquired for FT-NIR spectroscopy are indicated (white dots). (d) Intensity of clay absorption at 2207 nm from the OTR Holocene-LIG core. Only pixels where clay absorption was detected were mapped in this image. The vertical white line marks the boundary between the Holocene and Pleistocene portions of the core.

Figure 11. Pixel spectra from areas of the OTR Holocene-LIG core identified by AFE-2 analysis as having absorptions at ~2157 (blue symbols) or ~2207 (green symbols) indicative of calcite or Al-OH clay (kaolinite), respectively. Spectra from pixels where no absorption was found (black symbols) are indicative of aragonite. (a) Reflectance (2000–2500 nm) showing locations of the carbonate (CO$_3$) absorptions and Al-OH clay absorption. The wavelength range used for AFE-2 (2114–2255 nm) is indicated by the black bar at the bottom of graph. (b) Normalized reflectance spectra over the wavelength region used for AFE-2 (2114–2255 nm). Note that the discrete absorption doublet diagnostic for the clay mineral kaolinite becomes evident with its shortwave shoulder (at 2163 nm) being slightly longwave of the calcite feature at 2157 nm.
absorption maxima located at 2163 nm and 2207 nm, confirming that it was caused by the clay mineral kaolinite (Figure 11b; green symbols). Spectra where carbonate absorption was found had a single absorption at ~2157 nm but no Al-OH absorption (Figure 11a; blue symbols). The wavelength of this carbonate feature was close to the shortwave absorption minimum of the kaolinite doublet (at 2163 nm) but its shape was distinctly different to that of the kaolinite feature (Figure 11b; blue symbols). Spectra where no absorption was found were typical of aragonite (Figures 11a and 11b; black symbols). No kaolinite or other clay minerals were detected by XRD in any sample. Results from FT-NIR spectroscopy were entirely consistent with the results derived from AFE-2 (spectra shown in supporting information S2).

5. Discussion

5.1. Distinguishing Carbonate Minerals Using Feature Parameters of the Primary Carbonate Absorption

The carbonate classification method used in this study is based on the wavelength position and asymmetry of the primary carbonate absorption to identify and classify aragonite, calcite, and dolomite. Intensity was also mapped as an index of mineral abundance. The intensity of the primary carbonate feature in aragonite is smaller than in calcite or dolomite but it was rejected as a feature for distinguishing carbonate minerals because intensity can vary according to the abundance of a mineral or its crystallinity [e.g., Clark and Roush, 1984]. Spectral quenching effects due to organic matter also can have an impact on the intensity of the carbonate absorption [Crowley, 1986], although this was not tested for the samples in this study. Results show that large variations in intensity can occur in sections of core where variations in wavelength position and asymmetry were small, supporting the decision made on theoretical grounds not to use intensity as a parameter to classify the carbonate mineral.

The classified map of carbonate minerals derived from the hyperspectral image was validated against XRD results from selected areas on each core. In the PNG Porites coral, XRD results made across the aragonite-calcite boundary of McGregor and Gagan [2003] were in close agreement with changes in wavelength position and asymmetry and in the classified map of carbonates derived from them (Figure 6). In the OTR Holocene-LIG core, all of the areas classified as calcite or aragonite from hyperspectral imagery were entirely consistent with the dominant carbonate mineralogy as determined from XRD (Table 3). XRD analysis showed that the sample areas that were classed as dominantly calcite or aragonite from the hyperspectral imagery were, respectively, composed of 51–77% calcite or 83–92% aragonite. The two sample areas that had some proportion of their pixels classified as calcite (34–53%) and some as aragonite (11–29%) were considered to be a mixture of calcite and aragonite. XRD showed that these sample areas were composed of calcite (7–8%) and aragonite (81–82%). Both sample areas (sample # 11, 12) were located in a section of core where calcite and aragonite were heterogeneous in their distribution, making it extremely difficult to sample discrete areas composed entirely of either calcite or aragonite (cf., sample locations in Figure 1c with maps of calcite and aragonite made from hyperspectral imagery in Figures 8a, 8b, and 8d). This underscores the problems in making assumptions about spatial homogeneity of composition when sampling fossil reef cores. Both these sample areas had amounts of calcite (based on XRD) only slightly greater (2–3%) than the upper (1%) threshold commonly used as a cut-off for sample vetting for estimating chronology or paleoclimate variables, indicating that the technique was sensitive to small changes in amounts of calcite where amounts of calcite were small. XRD provides measurements of the amount of each mineral across the whole sample area, whereas hyperspectral imagery takes many hundreds or thousands of independent measurements over the same area. Spatial variations in mineralogy can therefore be detected at much smaller spatial scales than can be provided by physical sampling. This enables areas in the core that are shown to be homogenously composed of aragonite to be selected for geochemical analysis and dating.

Some areas within the PNG Porites coral and OTR Holocene-LIG core that had values of wavelength position or asymmetry that were intermediate between the values characteristic of calcite and aragonite were not classified by the algorithm. These areas had spectral characteristics that were consistent with mixtures of
aragonite and calcite and would not, therefore, be suitable for sampling. This indicates that the classification algorithm is adequately sensitive to identify areas of the core that were neither typical of calcite nor aragonite. For example, sections of the aragonite-calcite boundary in the PNG fossil Porites coral and sections B and C of the OTR Holocene-LIG core were not classified. In the PNG fossil Porites coral (Figure 5), this suggests that there is a zone where the carbonate mineralogy transitions from one composed dominantly of aragonite to another dominantly composed of calcite at the scale of individual pixels, as was observed in thin section [McGregor and Gagan, 2003]. It is worth noting that large changes in amounts of calcite determined from XRD were evident across sections of the transect where variations in wavelength position and asymmetry were relatively small (Figure 6). This was attributable to XRD measurements of calcite being determined from a relatively large volume of sample (each sample being 1–2 mm wide, 10–15 mm long, and 1–2 mm deep), and thus were an average value within this volume, whereas the hyperspectral measurements were acquired at the surface. The distribution of aragonite and calcite in the OTR Holocene-LIG core mapped by hyperspectral imagery is broadly consistent with a mapping made by visual inspection. Areas classified as calcite from the hyperspectral imagery was in some cases comprised of different material types as determined by visual inspection (e.g., see core sections I and N; cf., Figures 1c and 8d). This shows that calcite can be identified independently of the material types that comprise the core, an important point given that materials of different composition are commonly juxtaposed in cores across spatial scales ranging from mm to 10s of cm. By identifying areas suitable for dating, sampling can be precisely targeted to areas likely to yield the most accurate estimates. Importantly, areas of core identified as aragonite and suitable for sampling have been identified in areas of core of Pleistocene age. Such areas are commonly difficult to identify from visual inspection alone. The classification method presented here correctly identified all sample areas in the dolomitized cores as dolomite. Dolomitization of fossil coral cores is a less common process than the diagenetic recrystallization to calcite, yet can profoundly affect estimates of chronological age or SST.

The main focus of this paper was to provide a classified (i.e., a categorical) map of carbonate mineralogy by assigning a classification to each image pixel based on thresholds defined for the wavelength position and asymmetry of the primary carbonate absorption. Because these feature parameters are continuous variables that vary as a function of amount of calcite present in the sample, an alternative way of mapping a two-endmember system (e.g., a system where only calcite and aragonite were present) would be to estimate amounts of calcite directly from either wavelength position or asymmetry. Such estimates could then be used to provide quantitative information on the distribution of these minerals in the core. Many studies using chronological and paleoclimatological data derived from fossil corals in cores screen out areas that show any amount of calcite. This study has shown that where small (<13%) amounts of calcite are present, small increases in amounts of calcite from <5 to 7–13% caused relatively large changes in the wavelength position and asymmetry of the primary carbonate absorption feature (Figure 9). As amounts of calcite increase beyond 30%, wavelength position and, especially asymmetry, did not show further large significant changes. Thus, wavelength position and asymmetry are very sensitive to small increases in calcite where calcite is present in small amounts, but they become less sensitive where calcite is present in larger (>30%) amounts. This is significant because it is the small amounts of calcite that are easy to miss during vetting but have implications for the accuracy of estimates of chronology or other paleoclimatological variables, such as SST. Using the linear relationship between amount of calcite ≤13% and asymmetry, this study showed that calcite could be predicted to within ±2%. Although this regression approach was not used in this study to quantify amounts of calcite, our data show that it could be used to quantify small changes in calcite in samples. Further work, however, needs to be done to better describe the relationships between wavelength position and amounts of calcite ≤13%.

Water is present in many carbonate minerals and is particularly abundant, as fluid inclusions, in skeletal carbonates [Gaffey, 1988]. During diagenetic change, water inclusions in aragonite and water bound to carbonate minerals can be lost. Although water absorption in minerals can be easily detected and quantified from hyperspectral imagery [e.g., Murphy, 2015], it was not specifically considered as part of this study. Observations of water absorption made from the samples used in this study (data not presented) showed a significant reduction in water in areas of sample affected by diagenetic change. The use of water absorptions in spectra as a way of detecting diagenesis in skeletal carbonates merits further consideration.

The secondary carbonate absorption between 2156 and 2160 nm in calcite or at about 2140 nm in dolomite has the potential to distinguish calcite or dolomite from aragonite (using the AFE-2 analysis). The main
reason for using AFE-2 in this study was to identify and quantify absorptions related to aluminium clay minerals. However, the close proximity of the secondary carbonate feature to the Al-OH clay feature necessitated that it was considered in the analyses. Because aragonite does not have an absorption feature in this spectral region, the presence of aragonite in the core could be inferred by the absence of detectable absorptions. Areas mapped as having no absorption by AFE-2 (and inferred therefore to be aragonite) were spatially consistent with areas explicitly mapped as aragonite by AFE-1.

The ability of hyperspectral sensing to detect the presence of small amounts of calcite represents a promising new tool for prescreening coral cores for diagenesis prior to formal sampling of material for laboratory analysis. The spectral characteristics of calcite and dolomite are well described in the literature [e.g., Gaffey, 1985; Zaini et al., 2014]. However, this paper presents the first results showing how diagenetic changes can be detected and mapped in fossil reef cores, and particularly aragonite corals, as a way of improving sample vetting for the dating of cores and providing information about reef exposure and possible millennial sea-level oscillations. The method presented here is quick, relatively inexpensive, requires no a priori knowledge of the composition of the sample and can distinguish aragonite, calcite, and dolomite without the use of a spectral library. Future work will seek to determine if biogenic carbonate (i.e., coral aragonite) and abiogenic carbonate phases (i.e., secondary inorganic aragonite cement) are spectrally distinct, a possibility due to the porous nature of, for example, coral skeletons.

5.2. Distinguishing Aluminium-Rich Clay Minerals From Carbonates and Quantifying Their Abundance

Detecting clay minerals in fossil reef cores can provide important information on the depositional environment such as the influx of terrigenous materials [Saha et al., 2016 and references therein]. An aluminium clay mineral, kaolinite, was detected and quantified from hyperspectral imagery in some sections of the OTR Holocene-LIG core. Consistent with the findings of Crowley [1986], areas found to contain kaolinite were not visually distinguishable from other areas of the core, either in terms of color or brightness. XRD analysis from these sections of core also did not indicate the presence of kaolinite, probably because it was present in amounts below the levels of detection by that method. Further analysis of these samples by FT-NIR spectroscopy indicated the presence of kaolinite, supporting the results from the hyperspectral imagery. FT-NIR spectroscopy is particularly suitable for detecting kaolinite in amounts below the level of detection by XRD. Clay minerals, depending on the metal cation they contain, absorb in different locations in the spectrum between 2000 and 2500 nm. Aluminum clays absorb at about 2200 nm, but clays rich in other metals absorb at longer wavelengths [Bishop et al., 2008], specifically, Fe$^{3+}$ (2290–2310 nm), Mg (2330–2340 nm), and Fe$^{2+}$ (2350–2370 nm). In carbonate rocks, detecting aluminium clays is relatively straightforward because their primary absorption is at wavelengths away from the primary carbonate absorption between 2300 and 2350 nm. The present study shows that aluminium clays can be detected even where the weaker secondary carbonate absorption is present at about 2156–2160 nm. Absorptions caused by clays containing Fe$^{2+}$, Fe$^{3+}$, or Mg were not detected in any of the samples studied. Detecting these clay minerals is intrinsically more difficult in carbonate rocks because their primary absorptions are located across a range of wavelengths occupied by the intense primary carbonate absorption between 2300 and 2350 nm. The intensity of this feature would likely mask absorption features of Fe$^{2+}$, Fe$^{3+}$, or Mg clays, particularly if they were present in trace amounts [Pontual et al., 1997]. Further work is required to determine if clays containing these cations can be detected and quantified against a background of strong carbonate absorption. The ability of hyperspectral sensing to detect trace amounts of clay minerals, quantify their relative abundance and provide a spatial context to their distribution within reef cores, will provide important information about the location and nature of major unconformable surfaces (i.e., MIS1/MIS5) as well as changing depositional settings caused by the influx of terrigenous materials [Braithwaite, 2016; Woodroffe and Webster, 2014].

Although, other methods to quantify terrigenous materials in fossil coral reef cores do exist, e.g., ICP-MS (Ba/Ca, REE + Y), XRD, and XRF [Lewis et al., 2007; McCulloch et al., 2003; Saha et al., 2016], they are laborious and/or expensive and do not necessarily provide spatially contiguous measurements at submillimeter scales over large sections of core. Hyperspectral imagery therefore presents a practical method for rapidly, cheaply, and nondestructively quantifying aluminium clay over large sections of coral cores.

This study has shown how hyperspectral imagery can be used in studies seeking to reconstruct past environmental and climatic conditions from fossil reef cores, thus providing important information relevant to...
understanding the growth and demise of reef system. This approach provides a bridge between macroscale observations of fossil reef cores and those derived using discrete, analytical techniques (e.g., thin section petrology, SEM, XRD, XRF). As the cost of hyperspectral imaging systems continues to decrease and become more widely used, the methods presented here provide a solid framework for extracting information relevant to these research questions.

6. Conclusions

1. Aragonite, calcite, and dolomite can be distinguished and mapped in fossil reef cores using a combination of the wavelength position and asymmetry of the primary carbonate absorption between 2300 and 2350 nm.

2. A classification method was developed, which successfully detected diagenetic alteration of primary aragonite to calcite or dolomite in three different reef carbonate samples collected from different geological settings. Diagenetic changes, related to recrystallization of skeletal aragonite to calcite, were detected and mapped in the PNG P. coral core and in the OTR Holocene-LIG core. Dolomitization was correctly detected and mapped in the dolomitized coral core.

3. The wavelength position and asymmetry of the primary carbonate feature are extremely sensitive to changes in amounts of calcite in samples, where the amount of calcite is present in small amounts (≤ 13%).

4. Where calcite is present in small amounts (≤ 13%), relationships between asymmetry and amounts of calcite are linear enabling amounts of calcite to be predicted from asymmetry to within ± 2%. Further work is needed in determining the relationships between amount amounts of calcite ≤ 13% and, respectively, wavelength position and asymmetry. However, this approach shows promise for detecting small changes in calcite at concentrations relevant to sampling core material for laboratory analyses aimed at dating the corals or recovering geochemical palaeoenvironmental proxies.

5. Aluminum clay minerals, including kaolinite, were detected and their relative abundance quantified in the OTR Holocene-LIG core using the absorption near 2200 nm caused by Al-OH. Amounts of clay mapped from the hyperspectral imagery were below the limits detectable by standard XRD but their presence was confirmed by FT-NIR spectroscopy. The distribution of aluminum clay revealed that they were present exclusively in the LIG portions of the core.

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