Geochemical constraints on the temperature and timing of carbonate formation and lithification in the Nankai Trough, NanTroSEIZE transect

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ABSTRACT

Information about diagenetic processes and temperatures during burial of sediments entering the subduction zone is important for understanding changes in physical properties and seismic behavior during deformation. The geochemistry of authigenic carbonates from accretionary prisms can serve as proxies for conditions during carbonate cementation and resultant lithification. We report results from the Nankai accretionary prism recovered from Integrated Ocean Drilling Program (IODP) Sites C0011 and C0012 and we document continued cementation of deep sediment sections prior to subduction. Elemental and isotope data provide evidence for complex mixing of different isotopic reservoirs in pore waters contributing to carbonate chemical signatures. Carbon stable isotope values exhibit a broad range ($\delta^{13}\text{C}_{\text{V-PDB}} = +0.1$ to -22.5%) that corresponds to different stages of cement formation during burial. Carbonate formation temperatures from carbonate-clumped isotope geochemistry range from 16° to 63°C at Site C0011 and 8.7° to 68°C at Site C0012. The correspondence between the clumped-isotope temperatures and extrapolations of measured *in situ* temperatures indicate the carbonate is continuing to form at present. Calculated water

isotopic compositions are in some cases enriched in ^{18}O relative to measured interstitial waters suggesting a component of inherited seawater or input from clay-bound water. Low oxygen isotope values and the observed Ba/Ca ratios are also consistent with carbonate cementation at depth. Strontium isotopes of interstitial waters ($^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7059 to 0.7069) and carbonates ($^{87}\text{Sr}/^{86}\text{Sr}$ of 0.70715 to 0.70891) support formation of carbonates from a mixture of strontium reservoirs including current interstitial waters and relic seawater contemporaneous with deposition. Collectively our data reflect mixed sources of dissolved inorganic carbon and cations that include authigenic phases driven by organic carbon and volcanic alteration reactions. Physical properties of input sediments continue to undergo modification by carbonate cementation at present. Due to ongoing recrystallization, temperatures from carbonate-clumped isotopes reflect the modern geothermal gradient and may serve as useful measures of geothermal gradients in other siliciclastic basins where carbonate cementation occurs. We conclude that clumped-isotope signatures in authigenic carbonates from accretionary prisms are important proxies for the timing and conditions of cementation in active margins. Our results highlight the importance of using multi-proxy approaches to elucidate the history of carbonate cementation, particularly to establish carbonate precipitation at depth and its potential impact on the physical and mechanical properties of the sediment prior to subduction.

1. Introduction

The study presented here is part of the larger NanTroSEIZE (Nankai Trough Seismogenic Zone Experiment) Project to characterize inputs and deformation at a margin known for large, historical earthquakes and related tsunami generation (Tobin et al., 2009). Our results characterize sediment inputs in the Shikoku Basin (Fig. 1) and provide a baseline for comparison as the inputs evolve during deformation. Of particular importance are the mineralogy and physical properties of the sediments that can potentially become the focus of concentrated shear along major faults. Physical properties are related to lithology (including clay mineralogy), degree of lithification (cementation, compaction, consolidation), fluid content and fluid pressure (Moore and Saffer, 2001; Saffer and Tobin, 2011; Saffer and Wallace, 2015). Unlithified sediments high in smectitic clay minerals may release accumulated stress by slow slip and seismic tremor. Lithified sediments are more likely to store larger stresses before rupture and thus generate large, hazardous earthquakes (Saffer and Wallace, 2015).

Authigenic carbonate is known to form in marine sediments when diagenetic reactions result in supersaturation of carbonate minerals, and constitutes a significant component of the global carbon inventories (Wallmann et al., 2008; Wehrmann et al., 2013;

Schrag et al., 2013). Authigenic carbonates are produced from early reactions associated with organic matter decomposition via sulfate, manganese, and iron reduction, and as methane-derived carbonates from anaerobic oxidation of methane (AOM). For example, carbonates recovered from cold seeps on the Nankai accretionary wedge have strongly depleted $\delta^{13}\text{C}$ ratios (-36‰ to -56‰ V-PDB; Vienna PeeDee belemnite), suggesting that a component of the carbon was derived from AOM (Sakai et al., 1992). In this and other accretionary wedges, carbonates recovered at greater burial depths commonly retain chemical and isotopic information of the shallow sediments in which they were formed as a product of carbon cycling reactions. Here we document that carbonate cementation may also be occurring deep enough in the sediment sections that it may impact the seismogenic behavior along the plate boundary.

Alteration of sediment along continental margins leads to carbonate formation by a reaction transforming reactive silicates and volcanic ash to clay minerals, and releasing calcium, silica, other cations, and bicarbonate to the pore fluids (Wallmann et al., 2008; Wehrmann et al., 2013; Solomon et al., 2014). Formation of carbonate minerals driven by submarine silicate weathering can consume up to a third of buried carbon at continental margins, and may be as significant in sequestering CO_2 as weathering on land (Wallmann et al., 2008). This process is also occurring in the Shikoku Basin, where unstable volcanic matter is abundant (Figs. 1 and 2; Saito et al., 2010; Henry et al., 2012). In the Nankai input sites an additional source of calcium supplied by diffusion from the underlying oceanic basement further supersaturates formation fluids with respect to calcite.

We explore the amount, timing, chemical conditions, and temperatures related to cementation in the incoming sedimentary section of the Shikoku Basin before it enters the zone of megathrusting in the Nankai Trough subduction system. We use the mineralogy and geochemistry of carbonate minerals and interstitial waters, including traditional and carbonate clumped isotope analysis, to document that alteration of volcanoclastic material below the sulfate-methane transition zone (SMTZ) leads to formation of significant authigenic carbonate deep within the sediment column. As such, we provide the first evidence of carbon sequestration in deep-seated carbonate cements, which are partially triggered by weathering of volcanoclastic sediment below the SMTZ. We will show how carbonate-clumped isotope temperatures (Eiler, 2007) can help to constrain the timing of carbonate formation, and provide evidence that the carbonate clumped isotope composition of these carbonates may act as a proxy for the modern geotherm. We show small but significant degrees of carbonate cementation, which if continuing during burial can significantly strengthen the sediment (Sample, 1990). In addition, direct borehole measurements of temperature, together with clumped isotope measurements, provide a

direct constraint on which clumped isotope temperature calibration is most reasonable for the Nankai Trough input sites. Finally, we will discuss how these results are important for contributing to our understanding of fault behavior within the deep accretionary prism, the target of future drilling. Our study focuses on a major convergent margin, but the results may be applicable to other siliciclastic-dominated sedimentary basin where carbonate cements are forming, including petroleum provinces and passive margins.

2. Overview of Drilled Sites

Sites C0011 and C0012 (IODP Expeditions 322 and 333) were drilled in the Shikoku Basin to characterize the incoming sedimentary section, 21 and 30 km southeast of the deformation front, respectively (Fig. 1). The sites share similar sedimentary lithologies. The dominant sediments are bioturbated, fine-grained muds and silts and their lithified equivalents, locally with intervals of abundant volcanic ash or volcanoclastic sediment layers (Fig. 2). The sedimentary section at Site C0011 on the flank of Kashinosaki Knoll is nearly double the thickness found at C0012, at the knoll's crest (Saito et al., 2010; Henry et al., 2012). Lithologic units have been correlated between the two sites. Lithologic Unit I (~7.6 to 7.8 Ma at its base) includes numerous beds of reworked volcanic ash. Ash in Unit IB shows evidence of significant alteration at Site C0011 (Henry et al., 2012; Joseph et al., 2013a). Unit II is 9.1 to 9.4 Ma at its base, and along with hemipelagic mudstone contains volcanic sediment in the form of tuffaceous and volcanoclastic sandstone. Unit III is hemipelagic mudstone ranging from ~9.1 to 12.5 Ma in age and is relatively free of volcanic input. Unit IV comprises dominantly mudstones and siltstones. Sandy turbidites present in Unit IV at Site C0011 are not found at C0012. The lack of this more permeable lithology may serve to hydrologically isolate C0012 from subsurface fluids expelled at the deformation front, because at C0012 there is not a permeable pathway for fluid flow (Saito et al., 2010). Unit V is the deepest unit at C0011 and only the upper portion was cored due to failure of the drill bit. Sediment recovered from Unit V at Site C0011 contains volcanic ash layers. These ash layers are also observed in Unit V at C0012, which in addition contains abundant siliciclastic and volcanoclastic sandstone layers. The oldest sediment cored at C0011 is >14.0 Ma. Drilling at C0012 penetrated to basement and includes an additional unit (VI) comprising calcareous claystone. The sediment-basement contact was cored in numerous holes and yielded an age based on nannofossils of > 18.9 Ma. Abundant smectite in the Shikoku Basin sediments is indicative of alteration products of volcanic glass (Saito et al., 2010; Henry et al., 2012), an alteration that may play a role in formation of diagenetic carbonate during burial.

Carbonates occur throughout both sedimentary sections, averaging 3.6 wt% at Site C0011 and 4.4 wt% at Site C0012; carbonate abundances between 10 and 20 wt% are common in layers (Fig. 1; Expedition 322 Scientists, 2010ab; Expedition 333 Scientists, 2012ab). Carbonate is most abundant in approximately the upper third of the sections, with the exception of high carbonate abundances in the calcareous claystone at the base of Site C0012. Deposition of most sediment in deep water results in poor preservation of calcareous nannofossils and makes it highly probable that a large fraction of the carbonate in the cores formed through diagenetic reactions.

3. Methods

We used a combination of mineralogical and geochemical methods to explore characteristics of carbonate and interstitial water. Summarized here are the methods used for post-expedition analyses.

3.1. X-ray diffraction (XRD).

Carbonate mineralogy and abundance in 75 samples from Sites C0011 and C0012 were analyzed using a Siemens D500 diffractometer at Northern Arizona University (NAU; Appendix), at 43 kV and 38 amps. Runs were conducted at a step of $0.01^{\circ}2\theta$ and dwell time of 1 s. Peak heights for the main carbonate peaks were compared to in-house standards comprising powdered, acid-leached shale mixed with known amounts of calcite (Appendix). XRD is an efficient method for characterizing the bulk mineralogy of small sample sizes, but carbonate abundances obtained from this method have significant uncertainty, especially at low carbonate concentration (Expedition 348 Scientists, 2015a), and results presented here are considered semi-quantitative measures of relative abundances of different carbonate phases.

3.2. Scanning electron microscopy and electron probe microanalysis.

Fifteen samples were chosen for scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) analyses at NAU. The SEM is a JEOL 6480LV with backscattered electron detector (BSED) and Oxford energy-dispersive X-ray analysis system (EDS) used to determine semi-quantitative elemental compositions. EPMA used a Cameca SX-50 microprobe with beam current of 10 amps, voltage at 15kV, and a wide beam to minimize mineral damage. Carbonate standards were calcite, dolomite, siderite, rhodochrosite, and strontianite (Appendix). Chemical analyses by EPMA yield values accurate to within ~1-2 wt% relative.

3.3. Interstitial water stable isotope analyses (DIC-carbon and water $\delta^{18}\text{O}$).

The $\delta^{13}\text{C}$ composition of dissolved inorganic carbon (DIC) was obtained using a Gas-Bench II automated sampler interfaced to a gas source stable isotope mass spectrometer at Oregon State University (OSU) as described in Torres et al. (2005). DIC is allowed to evolve as CO_2 by addition of H_3PO_4 , and a known volume of dry CO_2 is transferred to a Finnigan DELTAplusXL mass spectrometer, which integrates the relevant isotope masses ($m/z = 44$, 45, and 46) as the CO_2 peak enters the source. The precision of the $\delta^{13}\text{C}$ measurements based on replicate analyses of a NaHCO_3 stock solution is better than $\pm 0.1\text{‰}$.

At Institut de Physique du Globe de Paris, the oxygen isotope compositions of fluid samples were measured using a GC-IRMS (AP2003) after equilibration of an aliquot (0.8 mL) of water sample with a $\text{He}+\text{CO}_2$ gas mixture. The measurements were calibrated using a set of water standards to provide $\delta^{18}\text{O}$ versus the V-SMOW (Vienna Standard Mean Ocean Water) standard scale. Measurements of $\delta^{18}\text{O}$ were determined with an analytical accuracy of better than $\pm 0.1\text{‰}$.

3.4. Carbonate elemental and isotope geochemistry

For samples analyzed for elemental ratios, 10 mg of powdered sample were weighed and transferred into an acid-clean Teflon vial, to which 3 mL of 4N HNO_3 was added to dissolve the carbonate. An additional 3 mL of 4N HNO_3 was added if the original volume failed to dissolve the whole carbonate component of the sample. Acidified samples were then centrifuged and prepared for ICP-OES analysis at OSU. Calibration was done against a series of mixed standards containing Ca, Mg, Sr, Mn, and Ba in ratios expected for methane-derived carbonates (e.g., Bayon et al., 2007; Torres et al., 2010). In addition, an aliquot of each sample was measured for Al to identify potential silicate contamination during acidification. Clay mineral contamination was less than 5% of the measured value in all samples.

For strontium isotope analyses, 10 mg of powdered sample was placed in an acid-washed Teflon vial and acidified with 4 mL of 25% (4 N) CH_3COOH . An additional 4 mL of 25% CH_3COOH was added if the initial volume failed to dissolve the whole sample. This solution was then refluxed at 70 °C for 12 h, sonicated for 30 min, centrifuged and decanted into Teflon vials. Strontium separation was carried out using a 50 μL Sr-specific column and resin from EICHRON. Isotopic analysis of a solution containing 300 ng Sr was performed using the Nu Plasma multicollector inductively coupled mass spectrometer (MC-ICPMS) housed in the W.M. Keck Co-laboratory for Plasma Spectrometry in the College of Oceanic and Atmospheric Science at OSU. $^{87}\text{Sr}/^{86}\text{Sr}$ data were normalized to NIST standard NBS 987, with a reported $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.710245 (Table 1; Joseph et al., 2013a). A

mean value of 0.710225 ± 0.000052 (2σ mean; $n = 91$) was obtained for repeated measurements. Replicate analysis of an in-house standard yielded a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.708170 ± 0.000051 (2σ mean; $n = 79$).

Samples selected for carbon and oxygen isotope analyses at NAU were powdered in a synthetic sapphire mortar and pestle and weighed into Labco Exetainer® vials for a target mass of 250 micrograms of carbonate per sample. Samples were purged with helium and reacted with 103% phosphoric acid for ~1 hour at 70°C, and the CO_2 gas was introduced with a helium carrier to a Finnigan Gasbench II where it is separated from water vapor and N_2O gas. Masses 44, 45, and 46 were then measured with a Finnigan Delta Plus isotope-ratio mass spectrometer in the NAU Colorado Plateau Stable Isotope Laboratory. $\delta^{13}\text{C}$ data were normalized using NBS-18, NBS-19 and LSVEC standards. $\delta^{18}\text{O}$ data were normalized using NBS-18 and NBS-19 standards. Analytical uncertainties are typically less than $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (1σ).

3.5. Carbonate clumped isotope geochemistry.

The abundance of the clumped $^{13}\text{C}\text{-}^{18}\text{O}$ bond in the species $^{13}\text{C}\text{-}^{18}\text{O}\text{-}^{16}\text{O}$ is reported using the variable Δ_{47} . Specifically Δ_{47} is defined as:

$$\Delta_{47} = \left[\frac{R^{47}}{2R^{13} \cdot R^{18} + 2R^{17} \cdot R^{18} + R^{13} \cdot (R^{17})^2} - \frac{R^{46}}{2R^{18} + 2R^{13} \cdot R^{17} + (R^{17})^2} - \frac{R^{45}}{R^{13} + 2R^{17}} + 1 \right] \cdot 1000$$

where R refers to the ratio of the minor isotopologue to the major isotopologue of the molecule (or atom) of interest (Eiler and Schauble, 2004). Δ_{47} measurements were made on 10 samples each from sites C0011 and C0012 using three different mass spectrometers with similar results: a specially modified Thermo Fisher MAT 253 gas source mass spectrometer and a Nu Perspective IS in the Tripathi Lab at the University of California, Los Angeles (UCLA); and a Thermo Fisher MAT 253 mass spectrometer at Caltech (Table 2). A brief description of the procedures is below and a more in-depth description is published elsewhere (Huntington et al., 2009; Passey et al., 2010; Tripathi et al., 2010; Loyd et al., 2012).

Sample and standards were processed using custom-built automated systems for digestion and purification attached to each gas source mass spectrometer that has been configured for the analysis of multiply substituted isotopologues of CO_2 (after Passey et al., 2010). The carbonate sample digestion system is composed of 1) a stainless steel autosampler that will hold high vacuum, 2) a common acid bath for phosphoric acid digestion of samples, 3) cryogenic traps (dry ice and ethanol, and liquid nitrogen) for the purification

and collection of CO₂ and removal of water and other gases with low vapor pressures, 4) a gas chromatograph with a packed column and a cryogenic trap to further purify CO₂ through the removal of organic contaminants, with helium being used as a carrier gas, with a flow rate of ~25 mL/min, 5) cryogenic traps to separate prepared gases from the helium, 6) a final set of valves and traps to purify CO₂ and transfer it into the bellows of the mass spectrometer. In this system, powdered samples with a carbonate mass of 8 mg are digested at 90°C in phosphoric acid ($\rho = 1.94$ g/ml; 105 wt%) in order to ensure a sufficient amount of CO₂ for stable voltages over the course of several hours. The reaction time was 20 minutes in a common acid bath system, with acid changed after every 10-15 analyses. Most samples were calcite or calcite with minor dolomite or rhodochrosite-siderite (R-S). There are four samples with the highest abundances of dolomite plus siderite range over 40-85 wt% of these phases. Twenty minutes has been shown to be sufficient reaction time for dolomite (Defliese et al., 2016). A previous study of clumped isotopes of siderite used longer reaction times (Fernandez et al., 2014), but to our knowledge no studies have been done on the R-S solid-solution. The R-S occurrences are typically as small, widely disseminated crystals 1-5 μ m (Fig. 3) that are likely to dissolve rapidly, but it is uncertain if complete dissolution of the R-S phase occurred. There is no evidence for artefacts in the data related to partial dissolution, since with only one exception, the results from the four high R-S samples do not differ significantly from calcite-dominated samples nearby in depth. A geological explanation for the exceptional sample is presented in the Discussion section.

The resultant gas from the acid bath was immediately sent through a glass water trap immersed in a dewar of ethanol/dry ice at -70°C, and CO₂ frozen in a second metal trap immersed in a dewar of liquid nitrogen. After two rounds of cryogenic purification to remove water, CO₂ is then passed through a gas chromatograph containing a column filled with PoraPak Q that is at -20°C, and then recleaned cryogenically as described above to remove any additional water before being transferred to the inlet of the mass spectrometer. Measurements are made to yield a stable 16-volt signal for mass 44, with peak centering, background measurement, and pressure balancing before each acquisition.

At UCLA, an “absolute reference frame” (ARF) was developed by analyzing CO₂ gas with different bulk isotope compositions equilibrated at multiple temperatures, and combined with carbonate standards to construct a secondary transfer function (Dennis et al., 2011). At Caltech, data were transferred to the ARF by use of two carbonate standards (Carrara Marble and TV01) and the use of a 1000° C equilibrated gas line, similar to prior studies where two equilibrated gas lines were not established (Dennis et al., 2011). Equilibrated gases are prepared at 25°C by exchange with H₂O, and at 1000°C by sealing in a quartz tube and heating in an oven for a minimum of two hours, followed by quenching at room

temperature. Standard gases are then purified and analyzed using the same protocol as sample gases. Approximately two to eight sample analyses and a minimum of three standard analyses (both gas standards and carbonate standards) were performed each day, depending on instrumentation. All carbonate data use the Henkes et al. (2013) acid digestion fractionation factor of 0.092‰, that was generated on the same type of instrumentation as ours, to normalize to 25°C; Defliese et al. (2015) report an acid digestion fractionation factor for Δ_{47} of 0.082 per mil at 90 deg. C, with an error of +/- 0.014 per mil (2 standard deviations) that is statistically identical to the value from Henkes et al. (2013). Both papers use a common acid bath system for the 90° C reactions, which justifies the choice of fractionation factor.

All Δ_{47} data in tables and figures are reported on the absolute reference frame. Uncertainties in reported Δ_{47} values and calculated temperatures include the propagated uncertainty in equilibrated gas determination and in sample measurement (Huntington, et al., 2009).

At UCLA we repeatedly ran a Carmel Chalk standard and determined an average Δ_{47} value of $0.683 \pm 0.005\text{‰}$ (1 s.e.) at UCLA (compared to a nominal value of 0.697‰ based on analyses by Tripathi at Caltech), a Carrara Marble standard with a value of $0.397 \pm 0.009\text{‰}$ (1 s.e.) (compared to a measured value of 0.397‰ from analyses at Caltech), and a TV01 standard with a value of $0.720\text{‰} \pm 0.012$ (1 s.e.) (compared to a value of 0.713‰ measured at Caltech).

Precision over the two months that analyses were made for this project, as determined on replicate analyses of standards, is 0.005 to 0.009‰ (1 s.e.), consistent with other studies (Eiler, 2007; Huntington et al., 2009; Eagle et al., 2010, 2011, 2013; Tripathi et al., 2010; Thiagarajan et al., 2011; Rosenheim et al., 2013). For analyses with more than one replicate all errors are based on external error. For a single replicate, the error is based on internal error. In order to monitor the presence of clean CO₂ samples, we screened for the presence of contaminating molecules such as hydrocarbons and sulfur compounds using mass 48 anomalies.

Temperatures are calculated using a published calibration equation (Tripathi et al., 2015) for inorganic calcite data that was recalculated on the absolute reference frame (Dennis et al., 2011). This temperature calibration was generated using the same instrumental set-up as used for the measurement of samples in this study. The uncertainty in temperature includes the standard error for individual measurements and the standard error between replicate analyses. Similar temperature results are obtained using the calibration of Ghosh et al. (2006). Other calibrations (Tang et al., 2014; Kluge et al., 2015; Defliese et al., 2015) yield high temperatures of formation relative to the modern geothermal gradient. All

temperature calibrations are calculated or re-calculated using a 25-90 °C acid fractionation factor of 0.092‰, identical to what was used in this study, and calibration equations and temperature calculations are provided in the Appendix.

The uncertainty in calculated water isotopic composition includes the internal error in temperature measurements for single replicates or external error for multiple replicates, and the uncertainty in measured $\delta^{18}\text{O}$ values of carbonates.

4. Results

We present mineralogical, textural, and geochemical data from secondary carbonates found in both input sites, which are compared to chemical data from interstitial waters (IW). The results place constraints on mechanisms and relative timing of formation of secondary carbonates.

4.1. Diagenetic carbonate textures and element chemistry.

Multiple mineralogical phases of carbonate are found in input sites C0011 and C0012. Evidence presented below suggests carbonate precipitated over a prolonged burial history. Carbonate abundances in samples for the present study range from 2.1 to 15.4 wt%, with two outliers of 36.7 wt% and 83.6 wt% (Appendix). There is no downhole trend of abundance in our samples for either site. High abundances are also found in pelagic calcareous claystone at the base of the sedimentary section in C0012 (Figs. 1 and 2).

We analyzed mineral and elemental compositions of carbonates to understand the mechanisms of cement formation and post-depositional alteration associated with the carbonate record (e.g. Pingitore, 1978; Veizer, 1983; Tucker et al., 1990; Bayon, 2007). Calcite is the most abundant carbonate cement, found in 67 of 75 samples examined. It is the dominant carbonate in two-thirds of the samples (Appendix). XRD patterns show a shift to higher values of the primary calcite peak from $29.4^\circ 2\theta$ in several samples. Typically the shift has been attributed to substitution of MgO for CaO in the calcite structure. But microprobe analyses of selected samples in our study shows MnO substitution and to a lesser degree FeO substitution in calcite is most commonly responsible for the shift (Appendix). Average MnO concentrations in main calcite cements are 3.6 to 13.2 wt%. In the rest of the paper we refer to calcites and Mn-calcites together as calcites.

The second most common carbonate phase is represented by a solid solution between rhodochrosite and siderite (Appendix; hereafter designated as “R-S”), which can be identified by one or more peaks between $\sim 31.5^\circ$ and $32.0^\circ 2\theta$. The primary peak locations for rhodochrosite and siderite are 31.45° and $32.00^\circ 2\theta$, respectively. Evidence for R-S is found in 41 samples, and it is the dominant carbonate in 11 samples; only one of the latter

was analyzed for clumped isotopes. The phase is typically too small to analyze with the microprobe (Figs. 3 and 4); the compositions of three samples are summarized in the Appendix. R-S also contains small amounts of MgO. Dolomite is present in 9 of 75 samples examined and dominant in only four. Siderite is a rare phase locally associated with pyrite.

Textural evidence provides evidence of co-precipitation of calcite and R-S. Calcite typically occurs as 20-50 micrometer ellipsoidal clots in a matrix of clay minerals (Fig. 3). Small ($< 5 \mu\text{m}$) crystals of isolated, idiomorphic R-S, and locally quartz, also occur in the larger calcite clots. Both calcite and R-S also are dispersed as small crystals in the clay matrix. The cores of R-S crystals in the matrix may be partially dissolved to develop secondary porosity. In other samples both calcite and R-S partially replace volcanic ash shards (Fig. 3). These textures suggest that calcite and R-S crystallized together. The trace element chemistry indicates manganese and iron were readily available in reduced form in pore waters during neocrystallization or recrystallization of carbonates. Dolomite was not found *in situ* by SEM, and its relationship to other authigenic phases is unclear.

There are no apparent trends in mineralogy with depth (Figs. 5 and 6). At C0011 calcite dominates the assemblages at all levels. R-S becomes increasingly common below 400 mbsf, as a nearly pure phase or as a minor phase with calcite. The R-S at depth may be a relict of carbonate formed at shallower depths (see section 4.2.1 below). At C0012 the pattern is reversed; R-S is more abundant in the upper 200 m of the section. In addition at this site dolomite is more common, but it is largely confined to an interval between 140 and 230 mbsf.

The Ba/Ca and Mn/Ca ratios for bulk leachates of carbonates and interstitial water concentrations are shown in Figure 7. The Ba/Ca ratio varies widely, both down-core and between sites. Barium incorporation into carbonate minerals is dependent upon barium availability in IW. The main source of dissolved barium in pore fluids is through dissolution of barite (Torres et al., 1996). Because barite dissolution occurs below the zone of sulfate depletion, high Ba/Ca levels in the carbonates indicate cement formation was below the SMTZ. The high abundance of manganese in carbonates is expected given the high concentrations of reduced manganese observed in interstitial waters. The availability of manganese likely results from alteration of volcanic matter, and reduction via active sulfur cycling by a microbial community (Torres et al., 2015). High abundance of Mn-bearing calcites is consistent with the observed Mn/Ca ratios in IW. It is notable that the trends in manganese concentrations are similar in carbonate and IW at Site C0012 from depths of 322 to 475 mbsf and may provide evidence of recent crystallization of these carbonates below the SMTZ (Fig. 7).

4.2. Carbonate isotope geochemistry

Carbon, oxygen, strontium, and clumped isotopes of carbonates are compared with modern interstitial water (IW) values to assess the degree of equilibrium between solid and fluid phases, and the conditions of carbonate formation.

4.2.1. Light stable isotopes ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and carbonate-clumped isotopes)

Stable isotope data indicate processes of carbonate precipitation, the temperature during precipitation, evolving isotopic compositions of the IW, and carbon cycling in the Shikoku Basin. Carbonate stable isotopes in the Shikoku Basin span a broad range from values expected of typical marine carbonates to those strongly depleted in ^{13}C and ^{18}O (Table 1; Figs. 5 and 6). The two Shikoku Basin input sites share some attributes. Both have a shallow population of samples with the least depleted isotopic ratios for carbon and oxygen in Lithologic Unit I. A deeper population of carbonates generally is more isotopically depleted.

4.2.1.1. Site C0011

At Site C0011 strong ^{13}C and ^{18}O depletions begin below 400 mbsf in Lithologic Unit II (Fig. 5). $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values range as low as -11.9‰ and -23.4‰, respectively. Although scattered, $\delta^{18}\text{O}$ generally shows a decrease in minimum values with depth. The oxygen isotope values could result from a combination of inputs from seawater, IW modified by water-rock interactions and alteration of sediment, and increasing temperature during burial. The samples strongly depleted in ^{18}O and ^{13}C require carbonate formation after significant modifications to seawater chemistry and possibly increased temperatures. The carbon isotopes of carbonates have a broad range of values that are lighter than dissolved inorganic carbon (DIC). With only a few exceptions in lithologic Unit IV, carbonates and DIC are not in equilibrium (Fig. 5).

Carbonate clumped isotope data provide quantitative measures of temperature and inferred $\delta^{18}\text{O}$ values of pore waters during carbonate formation. Samples with the greatest ^{18}O depletions were chosen for clumped isotope analysis; five samples with $\delta^{18}\text{O}$ values > 1‰ were also analyzed (Table 2; Fig. 5). For the calculated temperatures we used the temperature calibration of Tripati et al. (2015). Temperature calculations for other calibrations are also shown in the Appendix. Four analyzed samples are calcite with some MnO substitution, four are dominantly calcite with significant R-S, and one is a 50:50 mixture of calcite and R-S. We were unable to target individual carbonate phases and generations for analysis due to the dispersed nature of cement within the samples. Direct evaluation of mineralogical effects on clumped isotope temperatures and possible mixing relationships

(Defliese and Lohmann, 2015) therefore is not possible, but the temperatures of bulk samples do not show any systematic dependence on mineralogy.

The modern geotherm is shown for comparison with carbonate-clumped temperatures (Fig. 5). Generally clumped-isotope temperatures at C0011 lie very close to the geotherm, regardless of mineralogy. This is true even for three samples relatively undepleted in ^{18}O at 125, 250, and 269 mbsf. Three samples between ~600-700 mbsf plot significantly to the left of the geotherm. These include calcites with 13-22 wt% R-S, and one R-S with 15 wt% calcite. The temperatures lower than the geotherm could result from partial preservation of early-formed carbonate cement formed at shallower depths and subsequent burial. In general, however, the clumped-isotope results indicate the carbonates formed at temperatures similar to those found at their current depths.

The $\delta^{18}\text{O}$ values of fluids C0011 derived from clumped temperatures and inferred to be in equilibrium with the carbonates are shown in Figure 5D. To distinguish these waters from interstitial waters measured from core samples, hereafter we will refer to waters from clumped-isotope analysis as “clumped-water” isotope values. The clumped-water $\delta^{18}\text{O}$ values presented here are calculated assuming all carbonate is calcite and using the calcite-water fractionation expression of Kim and O’Neil (1997). The clumped-water isotopic compositions thus derived are heavier than current IW values. The differences range from 0-5‰ heavier within error for most carbonate samples. The actual difference is probably less because the carbonates are not pure calcite. The fractionation between carbonate and water is generally higher for minerals other than calcite, and with increasing substitution of MgO, MnO or FeO for CaO in the calcite structure. Accounting for these differences from pure calcite would lessen the isotopic difference between clumped fluid determinations and sampled interstitial waters. The correction can be as large as 3‰ for siderite (Carothers et al., 1988). For the sample dominated by R-S, a clumped-water $\delta^{18}\text{O}$ value corrected using the siderite-water fractionation expression of Carothers et al (1988) is shown in Figure 5. But the isotopic compositions of end-member carbonates are not known, and thus it is not possible to accurately calculate the $\delta^{18}\text{O}$ values of the clumped-fluid isotopic compositions to account for the effects of mixtures of carbonate minerals in all samples. The clumped-derived fluid isotope data are not likely to overlap completely with modern IW $\delta^{18}\text{O}$ values even if corrections were made for trace-element substitutions for CaO.

4.2.1.2. Site C0012

The ranges in carbon and oxygen isotopic data at Site C0012 are similar to those at C0011, but show some important differences (Fig. 6). Depletions of heavy isotopes of

carbon and oxygen begin at different depths. At Site C0012, ^{13}C depletions begin near the base of Lithologic Unit I (~139 mbsf), but strong ^{18}O depletions are not observed until near the base of Unit III (~330 mbsf). In the shallow group of carbonates, there is more scatter in $\delta^{18}\text{O}$ values, including a sample at 139 mbsf with the lowest observed $\delta^{18}\text{O}$ value for R-S at either site. The shallow group has the most dolomite-bearing samples, which have the highest oxygen isotope values. High $\delta^{18}\text{O}$ is commonly observed in dolomites forming in shallow carbonate crusts or as dispersed cements in the sediment column at continental margins above the SMTZ, where microbially-mediated carbon cycling occurs (Sample and Reid, 1998; Campbell et al., 2002). As with C0011, at C0012 the deeper population shows the greatest ^{18}O depletions, which occur in the calcite-dominated samples. The carbon isotope values range from slightly to moderately depleted. The carbonate carbon is also not in isotopic equilibrium with DIC carbon, with a few exceptions (Fig. 6). Although values are offset, carbonates in Units IV and V show parallel trends in $\delta^{13}\text{C}$ with DIC carbon.

Drilling at Site C0012 penetrated into basement, and we collected samples of the pelagic carbonate mudstone from just above the basement contact. These appear to retain their original isotopic compositions in carbon and oxygen expected for formation of carbonate tests from seawater. The lowest $\delta^{18}\text{O}$ value in C0012 was measured in a carbonate vein from the basement, and is the lowest $\delta^{18}\text{O}$ value of all samples analyzed. This sample will not be discussed further.

Clumped isotope measurements define a temperature array that is subparallel to the geotherm at Site C0012. With the exception of the mixed calcite/dolomite sample at 481 mbsf, all sediment samples lie very close to the downhole temperature gradient and are permissive of recent carbonate formation at or near current temperatures. The mixed calcite/dolomite concretion (45 wt% dolomite) yielded a clumped isotope temperature of 8.7°C (Table 2; Fig. 6). The temperature is consistent with carbonate formation above the SMTZ, which occurs at ~200 mbsf and coincides with a current temperature of ~30°C. Even though the thermal gradient at C0012 is significantly higher than C0011, the clumped-isotope temperatures at Site C0012 parallel the modern gradient.

The calculated clumped-water isotopic values for Site C0012 are shown in Figure 6. $\delta^{18}\text{O}$ values range from -5.2 to 4.9‰; most are < 0‰. As with C0011 the values for C0012 are mostly higher than modern IW $\delta^{18}\text{O}$ values. One carbonate sample overlaps the IW values, and six are within 2‰. Overall the difference between clumped isotope values and IW is smaller at C0012, which may reflect the greater abundance of calcite in these samples, suggestive of more complete recrystallization. The largest corrections related to mineralogy would result in decreases of 0.5 to 1.0‰ in the two dolomite-rich samples, at 147 and 481 mbsf, and the R-S-bearing sample at 69 mbsf. The correction shown for the dolomite sample

at 147 mbsf uses the dolomite fractionation expression of Vasconcelos et al. (2005). Even with corrections for mineralogy the clumped-water isotopic compositions would likely still be higher than $\delta^{18}\text{O}$ values of interstitial water. From these data it appears the carbonates did not form in oxygen isotopic equilibrium with current IW at some depths.

4.2.2. Strontium isotopes

Strontium isotopes of carbonates lie between modern interstitial water values and contemporaneous seawater values (Fig. 7). The $^{87}\text{Sr}/^{86}\text{Sr}$ range of carbonates at C0011 is 0.70777 to 0.70869. Over the depth range of analyzed carbonates, IW values exhibit a narrow range of 0.70672 to 0.70693. A similar pattern of carbonate values intermediate between IW and contemporaneous seawater is also observed at Site C0012, although here there is less scatter in the carbonate data, and IW and carbonate show a subparallel trend of decreasing $^{87}\text{Sr}/^{86}\text{Sr}$ with depth. Comparison of strontium with carbon and oxygen isotopes does not show a trend for either site (Appendix). Overall the results indicate the strontium pool in the diagenetic carbonates is a mixture of strontium from IW and seawater reservoirs.

In summary, the Shikoku Basin diagenetic carbonates exhibit variations in barium and manganese concentrations that reflect modern interstitial waters. The lowest $\delta^{18}\text{O}$ values are typically found in calcite-dominated samples. Temperatures from clumped carbonate analysis do not show a dependence on mineralogy. The clumped isotope temperatures are broadly aligned with the modern geotherm at each site, with some exceptions. The $\delta^{18}\text{O}$ values of waters derived from clumped isotope measurements generally are more ^{18}O -enriched than modern interstitial waters. Strontium and carbon isotopes of carbonates suggest a mixture of strontium and carbon reservoirs, including a component of interstitial water.

5. DISCUSSION

Carbonate cementation is an important active process throughout the entire section of Shikoku Basin sediments. The following discussion reconstructs the history of carbonate diagenesis based on geochemical and mineralogical data. The data provide constraints on the carbonate-forming process and have some important implications for characterizing temperature gradients and physical properties of sediments in subduction systems. The role of cementation and its relative depth within a formation determines whether cementation or compaction is the principal driver of porosity reduction. Cements alter the mechanical properties of the sediment, have a significant impact on its permeability, and thus affect fluid

flow. All of these cement-induced changes, especially when they occur at depth, will play a large role in the seismogenic behavior of the margin.

5.1. Timing of carbonate formation

Based on the stable isotopic results the carbonates can be subdivided into two major groups. The upper 300 m at C0011 and upper 150-200 m at C0012 have characteristics that can best be explained by relatively shallow, early-formed carbonates. Foremost are stable isotope signatures commonly associated with formation in waters that are not significantly different than the initial seawater composition. The decrease in $\delta^{13}\text{C}$ values beginning at 150 mbsf may correspond to ^{13}C -depleted carbonates forming just above the sulfate-methane transition zone (SMTZ), which is at ~200 mbsf (Fig. 6; Whiticar, 1999). Samples with combined calcite, dolomite, and R-S with these shallow isotopic characteristics is consistent with textural evidence of co-precipitation, and indicates most of the carbonates are diagenetic cements rather than carbonate tests from hemipelagic sedimentation. The second, deeper group is characterized by decreases in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values with depth. The steady decrease of $\delta^{18}\text{O}$ may result from a combination of increasing temperature and locally enhanced rates of alteration of volcanic matter to smectite at both sites (see below). The greater scatter in the deep group suggests some samples retain an early, undepleted $\delta^{18}\text{O}$ signature. A persistent ^{13}C depletion in the deeper group is expected for input of light carbon derived from the sulfate-reduction process above the sulfate-methane transition zone (SMTZ). Lowered values of $^{87}\text{Sr}/^{86}\text{Sr}$ in carbonates relative to contemporaneous seawater values present at the time of deposition in sites C0011 and C0012 at ~600 mbsf and ~200 mbsf, respectively, are consistent with input from the strontium reservoir derived from alteration of sedimentary volcanic matter (Fig. 7; Joseph et al., 2013a).

The carbonate clumped isotope data provide an important constraint on the timing of carbonate formation. At Site C0011 the 10 temperatures determined from clumped isotopes generally parallel the geothermal gradient. The geotherm is based on direct temperature measurements above 200 mbsf, yielding a gradient of 91°C/km, and is extrapolated to greater depth using measurements of thermal conductivity from core samples (Marcaillou et al, 2012); the temperature uncertainty increases with depth. Seven of the clumped measurements fall within 5°C of the extrapolated gradient, within clumped-isotope temperature uncertainties. There is a similar trend at Site C0012, even though the gradient is significantly higher (135°C/km). One exception is a carbonate concretion (C0012A-47R-2, 30-35 cm) with ~45% dolomite from a depth of 481 mbsf with only a slightly depleted $\delta^{18}\text{O}$ value. The sample appears to have retained some of its original chemical and mineralogical characteristics from early precipitation at a depth closer to ~40 mbsf. The other eight

sediment-hosted carbonates define a downward trend in temperatures that is also parallel to the temperature gradient (Marcaillou et al., 2012). Evaluation of mixing effects on clumped isotope temperatures is not directly possible in this case, but given the close match for most samples between calculated and measured water $\delta^{18}\text{O}$ values, there is unlikely to be a significant mixing offset. Any mixing offset that occurs will likely cause a slight decrease in measured clumped isotope temperatures versus real precipitation temperatures (Defliese and Lohmann, 2015), and would result in a closer match to the geothermal gradient. The geothermal gradients at the two sites are markedly different, yet the close correspondence between carbonate clumped isotope temperatures and the modern geotherms at each site is compelling evidence that ^{18}O -depleted carbonates of varying mineralogies have crystallized recently under current temperatures.

In addition to oxygen and carbonate clumped isotopes, the barium and manganese data support formation of many of the deeper Shikoku Basin carbonates below the SMTZ and possibly recently. Data from the Cascadia margin Site U1329 provide an interesting contrast (Joseph et al., 2013b). There carbonates inferred to have formed above the SMTZ and now found below that zone show little enrichment in the Ba/Ca ratios with depth, even though barium in the pore fluids below the SMTZ reaches concentrations $> 100 \mu\text{M}$ (Fig. 7). Above the SMTZ, where these carbonates likely formed, barium was sequestered into barite. In marked contrast, carbonate samples from the deeper portion of the Shikoku Basin do show considerable enrichment of barium. At Site C0011 Ba/Ca values in carbonates are as high 5.4 mmol/mol, consistent with precipitation at considerable depths where Ba in the pore fluids reaches $150 \mu\text{M}$. Carbonates from Site C0012 are also enriched in Ba/Ca (up to 2 mmol/mol) consistent with precipitation significantly below the SMTZ where dissolved Ba reaches $50 \mu\text{M}$ (Fig. 7). Parallel trends in manganese concentrations in carbonate and IW at Site C0012 also support recent carbonate formation at depth (Fig. 7). Mn/Ca ratios in carbonates decrease steadily from ~ 3 to ~ 1 ((wt% $\times 10$)/wt%) from 332 to 475 mbsf. A parallel decrease in manganese IW concentrations from $105 \mu\text{M}$ to $10 \mu\text{M}$ occurs in the same depth interval (Fig. 7). Four of the carbonate samples within this trend have carbonate clumped isotope data indicating recent carbonate crystallization, and we suggest the manganese concentration in these carbonates is also controlled by the attendant IW composition.

5.2. Carbonate formation process in the Shikoku Basin input sites

The mechanism of formation of diagenetic carbonates must explain the evidence from stable isotopes, temperatures derived from carbonate clumped isotope measurements,

and barium and manganese data for recent crystallization. In contrast, the strontium isotope data, and to some extent carbon isotopes, suggest that some carbonates retain a relic chemical signature from earlier formation. The carbonates with a “seawater” oxygen isotope signature at C0011 are dominated by carbonates with significant R-S content that suggests R-S is a favored early carbonate phase. The presence of calcite in the shallow group indicates multiple carbonates can form early in the burial history. The clumped temperatures derived from ^{18}O -depleted carbonates indicate that recent carbonate crystallization is dominant. We argue that the diverse mixture of carbonates in this deeper group of cements represents a continuum of carbonate cementation during burial in the Shikoku Basin, partially preserving relic early cements while forming dominant later cements. Greater prevalence of ^{18}O depletions of carbonates at C0012 indicates the relic shallow cement signal is less well preserved, suggesting recrystallization of early cements during burial is more important here. The following discussion will attempt to reconcile the multiple proxies for conditions of carbonate formation.

5.2.1 Role of carbon cycling

In marine sediments the lightest carbon available through carbon cycling is near the sulfate-methane transition zone (SMTZ; Whiticar, 1999). At Site C0011, the sulfate profile clearly demarcates the depth of sulfate depletion at ~80 mbsf. There are limited data available for $\delta^{13}\text{C}$ values of dissolved inorganic carbon (DIC), but clearly the deeper carbonates have a carbon isotopic composition that is depleted in ^{13}C relative to the concomitant seawater, suggesting some carbonate found deep in the basin precipitated at shallow depths where presumably there is a more ^{13}C -depleted DIC pool.

At Site C0012 a similar relationship exists between carbonate carbon and DIC. Near parallelism of the depth trends of $\delta^{13}\text{C}$ suggest a possible relationship between the two, but the carbonate carbon is lighter than would be expected for equilibrium with the $\delta^{13}\text{C}$ -DIC (Fig. 6). It is notable that the $\delta^{13}\text{C}$ minimum in sample C0012A-46R-CC, 36-40 is at a similar depth to a minimum in $\delta^{13}\text{C}$ -DIC. This deep depletion in ^{13}C corresponds to a zone of deep methane oxidation supported by sulfate diffusion from the underlying basement (Torres et al., 2015). Taken together the carbon isotope characteristics of the carbonate minerals and DIC suggest the deeper, recrystallized carbonate retained an inherited signal of light carbon from early, shallow initial formation, but is also influenced by more recent processes.

Carbonate formation driven solely by carbon cycling in accretionary margins has been well documented by analyses of samples recovered from the seafloor as well as shallow and deep sediments (e.g., Ritger et al., 1987; Bohrmann et al., 1998; Wallman et al., 2008; Wehrmann et al., 2013). These carbonate phases record conditions at and below the

SMTZ, where organic carbon cycling reactions are more prevalent (Whiticar, 1999), and can result in a broad range of strongly depleted to enriched carbon isotopes (e.g., Sample and Kopf, 1995).

The situation in the Shikoku Basin is, however, more complex. Here, in addition to carbon cycling processes, alteration of volcanic matter and calcium diffusion from basement drive the system toward additional carbonate precipitation. This could explain the lack of correlation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values. Whereas oxygen and carbon are initially controlled by low-temperature alteration of sedimentary volcanic matter, there are additional changes in the carbon isotopic composition due to carbon cycling driven by sulfate diffusion from the basement aquifer (Torres et al., 2015).

We argue that ash alteration in the Shikoku basin in the zone where methanogenesis produces CO_2 results in a release of cations (Ca, Mn, Fe) and bicarbonate that drive carbonate cementation at depth as described by Wallmann et al, (2008) and summarized as:

cation-rich silicates (e.g., volcanic matter) + CO_2 + K^+ $\rightarrow$

cation-depleted silicates + HCO_3^- + Na^+ + Mg^{2+} + Ca^{2+} + Mn^{2+} + other cations (1)

This reaction and an additional Ca^{2+} source from diffusion from basement promotes saturation with respect to carbonate in pore waters. Given the changes in the pH of IW, carbonate diagenesis at depth may be occurring by dissolution and reprecipitation. The process could account for the lower carbonate abundance at greater depths in both sites (Fig. 1), as the amount of carbonate dissolved in the zone of methanogenesis is not balanced by cement formed during *in situ* silicate weathering.

5.2.2 Strontium isotope constraints on carbonate recrystallization

In contrast to the carbon and oxygen isotope and temperature data, strontium isotopic compositions of the cements cannot be explained as crystallization in equilibrium with current interstitial waters. The cements are isotopically more radiogenic than coexisting IW, but lower than seawater $^{87}\text{Sr}/^{86}\text{Sr}$ values contemporaneous with the depositional ages of sediment (Fig. 7). This contrasts with the results from Cascadia Site U1329, where strontium isotopic compositions of cements are consistent with precipitation in contemporaneous seawater, except for the two deepest samples, which reflect precipitation driven solely by lateral flow of exotic fluids within a deep conglomerate (Joseph et al., 2013b). In the Shikoku Basin, the interstitial water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are controlled by mixing of three components: modern seawater, strontium from alteration of volcanic ash, and diffusional communication

with basaltic basement (Joseph et al., 2013a; Torres et al., 2015). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for ash (~0.706; Joseph et al., 2013a) dominates the IW from 434 to 850 mbsf at Site C0011, and 180 to 417 mbsf at Site C0012. This trend in isotopic values indicates alteration of volcanic matter is particularly important in the interval where the carbonates analyzed in our study are concentrated. Above and below the interval of ash alteration, there is evidence for diffusive strontium exchange with seawater ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7902$) and basement ($^{87}\text{Sr}/^{86}\text{Sr} \sim 0.703$ to 0.705; e.g., Staudigel et al., 1981), respectively (Joseph et al., 2013a).

The carbonate strontium isotope values in our results can be explained as a mixture between relic strontium from initial crystallization and IW modified by alteration of volcanic matter. In a partially closed system the degree to which carbonates acquire new isotopic values will depend on a mass balance between strontium in the IW and the original carbonates. Over the depth range for which we have strontium data, pore water concentrations vary from 12.6 to 22.7 ppm (mean = 19.1 ppm). Strontium concentration data are not available for the carbonates, but concentrations in carbonates in the Cascadia accretionary prism at similar depths vary from 10.4 to 828 ppm (mean = 283 ppm; Sample and Kopf, 1995; Sample and Reid, 1998). In Nankai the water-rock ratios in pore space during recrystallization is not well constrained because the percent of space between grains filled by carbonate is not known. Simple mass balance models show that mixing of inherited strontium with contemporaneous seawater-like $^{87}\text{Sr}/^{86}\text{Sr}$ values during sediment deposition (0.7088) and IW $^{87}\text{Sr}/^{86}\text{Sr}$ modified by ash (0.7063-0.7070) can achieve the observed strontium isotopes in the carbonates, which mostly range between 0.7080 and 0.7086 (see Appendix). The strontium isotopic values measured in this study can be obtained for IW strontium concentrations of 20 ppm and initial carbonate strontium concentrations of 50-100 ppm. If higher strontium concentrations in the initial carbonate are assumed, relatively high water-rock ratios are required.

The mixing calculations support a carbonate-formation mechanism of local dissolution and re-precipitation in a closed system with respect to strontium, and provide support for the inference that there is little fluid flow in these input sites (Torres et al., 2015). Recrystallization of carbonates during burial in low-permeability sediment with minimal fluid flow can thus lead to re-setting of $\delta^{18}\text{O}$ and clumped isotope temperatures, but incomplete resetting of strontium or carbon isotopes. The former are controlled by temperature and the oxygen component of IW, while the latter depends on relatively low-abundance solutes (strontium, carbon) in IW. Resetting of clumped isotope temperatures by solid-state diffusion is not a plausible explanation given the low-temperature conditions well below the threshold required for diffusion to become important (Passey and Henkes, 2012; Henkes et al., 2014). The amount of fluid-carbonate isotopic exchange is negligible given the small water-rock ratios. We note that the deepest two samples in Site C0012 have $^{87}\text{Sr}/^{86}\text{Sr}$ values shifted

furthest from seawater toward strontium isotopic compositions similar to oceanic basement. These carbonates clearly have a smaller proportion of inherited strontium than other samples, and may represent a greater degree of neocrystallization.

5.2.3 Significance of clumped-water isotope values

Clumped isotope analysis allows determination of the isotopic composition of pore fluids at the time of carbonate formation (Eiler, 2011). In the Nankai input sites, the clumped-water $\delta^{18}\text{O}$ values are in some cases higher than measured modern fluids. Differences range from negligible to ~5‰ higher for clumped waters. Larger differences are found in two samples with high abundance of dolomite or rhodochrosite-siderite. After correction using appropriate fractionation factors (Carothers et al., 1988; Vasconcelos et al., 2005), these two samples have similar differences in the offset between IW and clumped-water $\delta^{18}\text{O}$ values as calcite samples. During low-temperature burial diagenesis at the input sites there are multiple processes that can enrich or deplete the fluids in the heavy isotope, ^{18}O . Precipitation of carbonate in isolated microchemical environments or movement of fluids vertically in the section may play a role in developing isotopic variation. Microchemical environments with fluid isotopic anomalies may not have been captured during shipboard sampling of interstitial waters that took place over core intervals of 19-48 cm (Expedition 322 Scientists, 2010ab).

The isotopic composition of carbonates and calculated clumped fluid isotopic values of carbonates is influenced by temperature and low-temperature diagenesis (Fig. 8; Eiler, 2011). For example, burial diagenesis of carbonates that remain in contact with open marine waters would follow a trend of increasing temperatures (decreasing Δ_{47}) and clumped fluid isotopic values that remain near 0‰. In closed systems we might expect the fluid isotopic compositions to evolve toward higher $\delta^{18}\text{O}$ values due to rock-water interactions. Pore waters in the Nankai input sites, however, can evolve to lower or higher $\delta^{18}\text{O}$ values with increasing burial due to competing processes of fluid-sediment interaction. Low-temperature alteration of volcanic matter to clay depletes ^{18}O in fluids (Gieskes and Lawrence, 1981). This process can continue to temperatures up to 150°C (Alt et al., 1986) and is likely responsible for the observed decrease of IW $\delta^{18}\text{O}$ values with depth. In contrast, diagenetic alteration of smectite to illite releases ^{18}O -enriched clay-bound water (Perry et al., 1976; Yeh and Savin, 1977; Primmer and Shaw, 1990) to mix with existing pore water. In most geologic settings this process becomes important at 60°C and can continue up to ~150°C (Pytte and Reynolds, 1988; Saffer et al., 2008).

The oxygen isotopic compositions calculated for clumped waters may reflect a mixture of waters from original seawater trapped during initial burial, clay diagenesis, and

alteration of volcanic matter. Of the 19 sediment cements we analyzed, five have clumped water isotopic values close to the interstitial water isotope values measured from core samples (Figs. 5 and 6). The five are consistent with fluids dominated isotopically by alteration of reactive silicates to clays. The remaining 14 samples are more enriched in ^{18}O than coexisting IW. Nearly all of these have clumped-water $\delta^{18}\text{O}$ values $\leq 1\text{‰}$. The exception is a dolomite cement. For the majority of samples a mixture of fluids between a marine endmember and lighter waters derived from the alteration of reactive silicates could explain the isotopic variations (Fig. 8). Alternatively, clay diagenesis resulting in enrichment of fluids in ^{18}O is most likely to occur near the bottom of each input site, where temperatures exceed 60°C , the threshold for the smectite-illite transition. For shallower samples with high clumped-water $\delta^{18}\text{O}$ values upward diffusion or advection of heavy waters is required. Possible chemical diffusion is indicated by chemical profiles such as chlorinity and sulfate (Torres et al., 2015). There are also trends toward slightly higher values near the base of the IW $\delta^{18}\text{O}$ profiles suggesting possible diffusion from deeper, heavier IW from an ^{18}O -enriched source.

An alternative explanation for enrichment of ^{18}O in clumped water isotopes is disequilibrium precipitation. Disequilibrium commonly results in low Δ_{47} and high temperatures relative to the observed conditions a variety of settings (Tripathi et al., 2005; Affek et al., 2008; Thiagarajan et al., 2011; Loyd et al., 2016) or predicted from theoretical calculations (Guo et al., 2009; Hill et al., 2014). Disequilibrium does not seem a likely explanation to explain results from Nankai input sites. Shallow carbonates formed at cool temperatures do not exhibit the expected anomalously low Δ_{47} values as might be expected. There are no systematic anomalies in clumped-water isotope values related to depth or temperature of formation. Carbonates in deeper samples formed at higher temperatures, conditions under which disequilibrium effects have not been observed in other settings.

Based on analysis of the mineralogy, and the downhole temperature trends in clumped temperatures and fluid isotopes, we conclude that cementation occurred generally in equilibrium with current downhole temperatures, in microchemical environments that are not well characterized with respect to oxygen isotope compositions by bulk measurement of interstitial water chemistry. Further work in volcanoclastic deep marine settings at other convergent margins and at deeper portions of the Nankai accretionary prism, utilizing smaller interstitial water samples in close association with cemented horizons, might clarify the relationship between clumped-water and *in situ* IW isotopes.

5.3 Carbonate formation history and relevance to properties of input sediments

The results of this study indicate carbonate formation is an important active process in the Shikoku Basin throughout burial and includes dissolution and re-precipitation at depth. Temperatures from clumped-carbonate isotope geochemistry show the prevalence of *in situ* carbonate dissolution and recrystallization or neocrystallization. The clumped data are supported by widespread ^{18}O -depleted cements and by textures showing partial dissolution of R-S (Fig. 3). As diagenesis of organic matter proceeds below the SMTZ, increasing carbon dioxide levels from methanogenesis lower the pH and induce at least partial dissolution of the carbonate (Fig. 9; Wallman et al., 2008). Local alteration of volcanic matter driven by changes in pH by methanogenesis can lead to local environments with increased alkalinity and carbon re-precipitation (reaction 1). Replacement textures of ash by calcite and R-S are observed in support of this mechanism (Fig. 3). The space occupied by individual clots of carbonate, with quartz inclusions, is consistent with nucleation and growth of new carbonate in space that is larger than original pore space, by reaction (1) involving replacement of volcanic matter. The result is formation of cement that is combined clay, carbonate, and to a lesser extent silica during burial diagenesis.

Carbonate-clumped isotope data support the recent timing of carbonate formation. Inferences about timing process depend in part on the Δ_{47} -temperature calibration chosen. For the carbonate-clumped temperature values we used the calibration of Tripathi et al. (2015). Using other calibrations (e.g., Defliese et al., 2015; Kluge et al., 2015) yielded higher temperatures for most samples, in many cases well above the measured geothermal gradients. The results from the Nankai input sites provide valuable information for evaluation of different clumped isotope-temperature calibrations. For our results we compared two calibrations (Tripathi et al., 2015; Tang et al., 2014; see Appendix). Both are based on measurements made on similar instrumentation, and both include measurements made at the UCLA lab also used for our study. The steep-sloped calibration curve has a narrower range of temperature values over the range of measured Δ_{47} values in this study (Tripathi et al., 2015). It yields somewhat higher temperatures at high Δ_{47} values, but for most samples the temperatures from this calibration are lower compared with the shallow-sloped calibration of Tang et al. (2014). Their calibration yields a larger range of temperature and higher temperatures for low Δ_{47} values. The steep-sloped calibration yields results most consistent with geothermal gradients at both input sites (Figs. 5 and 6). The calculated clumped water $\delta^{18}\text{O}$ values for this calibration are closer to measured, modern interstitial water $\delta^{18}\text{O}$ values as well. If the calibration of Tang et al. (2014) is used, more temperatures lie well above the geothermal gradients, and the clumped fluid $\delta^{18}\text{O}$ values are further from measured IW values. There is no clear evidence for widespread geothermal activity in the past that would account for the temperatures elevated about the current gradient. We

conclude that for carbonate diagenesis in these siliciclastic-dominated, deep-sea sediments, the calibration of Tripathi et al. (2015) is more reliable. Our results provide a new benchmark for clumped isotope temperature calibrations that can be tested with further studies from drilling in similar settings.

A powerful result from our study is the demonstration that clumped isotopes from carefully chosen samples can be used to determine successfully the geothermal gradient to oceanic basement where other more direct measurements may not be available. In general direct borehole temperature measurements subduction systems are limited to depths of a few hundred meters (e.g., Harris et al., 2011). The slightly elevated temperatures from the bottom of Site C0012 provide evidence that in the past, periodically warmer fluids escaped from the crest of the basement high at Kashinosaki Knoll into the overlying sedimentary column. The ability to constrain temperatures with clumped isotope data is a significant result, as temperature histories of buried, clay-rich sediments provide important information about the potential for clay mineral diagenesis, the development of related excess pore pressures, and the variations in seismogenic response of these sediments during faulting (Saffer and Wallace, 2015).

Carbonate cementation can also affect the physical properties of sediments and preserve information about the condition under which lithification occurs. In ancient convergent margins the chemistry of carbonate veins is an important proxy for changes in fluid sources, evolution of pore fluid pressure, and changes in strength parameters of sediments (Dielderfer et al., 2015). In active margins interseismic healing in faults by cementation results in an increase of fault strength due to an increase in the grain contact area and cohesion (Tenthorey and Cox, 2006; Ikari et al., 2016). Carbonate cementation can facilitate velocity-weakening behavior in a fault zone and interseismic recovery of strength, both characteristics of faults experiencing repeated seismic rupture (Chen et al., 2012; Ikari et al., 2016). As sediment enters the accretionary prism, the presence of carbonate cements like those documented here may enhance the probability for this strengthening effect where major faults localize in cemented horizons. Carbonate cementation driven by sub-seafloor alteration of volcanoclastic sediment locally composes 10-20% of the solids and may continue during subduction and accretion. Early results from drilling to depths of 3000 mbsf into the Nankai prism show that carbonates veins and cements are commonly associated with fault zones (Expedition 348 Scientists, 2015b).

CONCLUSIONS

Carbonate mineralogy, composition, strontium and stable isotope data, including carbonate clumped isotope thermometry, provide constraints on the mechanism and timing of carbonate formation in incoming sediments to the Nankai subduction zone. While

carbonate cements begin to form very early in the burial history, there is evidence from barium and carbonate-clumped isotope temperatures that carbonate continues to precipitate throughout burial. Other chemical data support retention of some of the early history of carbonate cementation in the recrystallized carbonate. The process of lithification due to carbonate cementation likely involves dissolution and re-precipitation under current temperature conditions. As is known for continental margins worldwide, carbonate formation can be relatively common above the SMTZ, where carbonate forms because sulfate reduction and anaerobic oxidation of methane result in an increase in alkalinity. Here we show that in addition to these early methane-derived authigenic carbonates, ash alteration at greater depths consumes protons released during methanogenesis, and thus constitutes an additional source of alkalinity (Wallmann et al., 2008). Added to this, there is a continuous supply of calcium by alteration of volcanogenic materials (ash and underlying basaltic basement) that maintains supersaturation with respect to calcite. The clumped isotope temperatures derived from samples ranging from 69 to 762 mbsf are in agreement with current temperature gradient estimates, documenting that the main fraction of the carbonate at depth formed *in situ*. The various temperature data indicate that the carbonate clumped temperature calibration of Tripathi et al. (2015) is most suitable for the Shikoku, and we believe will also apply to other siliciclastic, carbonated-cemented sedimentary basins. Our results highlight the importance of using multi-proxy approaches to elucidate the history of carbonate cementation, establish carbonate cementation at depth, and its potential impact on the physical properties of the sediment. We demonstrate that carbonate clumped isotope thermometry is a useful tool in constraining geothermal gradients in subduction systems.

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List of Tables

Table 1. Carbonate geochemical data.

Table 2. Carbonate clumped isotope data.

Figure Captions

Figure 1. Index map (A), seismic reflection profile showing locations of IODP Sites C0011 and C0012 (B), and shipboard total carbonate results (coulometric method) (modified from Expedition 322 scientists, 2010ab (diamonds) and Expedition 333 Scientists, 2012ab (circles)). Sediment cores were collected to depths of 881 mbsf at Site C0011 and 538 mbsf at Site C0012.

Figure 2. A. Lithologies from coring during Expeditions 322 and 333 (from Expeditions 333 Scientists, 2012b). Unit designations shown by Roman numerals next to lithologic columns. Diagonal-line patterns are slumped intervals. Depths in meters below seafloor (mbsf). Age-depth models based on nannofossils, magnetostratigraphy, and tephrochronology are shown in B.

Figure 3. Representative SEM-EDS spectra for solid solution rhodochrosite-siderite (R-S) (A) and Mn-calcite (B) from sample 322-C0011B-39R-2. Also shown are typical textures of secondary carbonate imaged by SEM backscattered electrons. C) Segregated clots of Mg-calcite (MC) and smectite (SM). D) Clot of Mg-calcite with idiomorphic solid-solution R-S and small inclusions of secondary quartz (Q). R-S also occurs in the smectite-rich matrix. E) Partial replacement (r) of volcanic ash and silicates by calcite (C).

Figure 4. Ternary diagrams showing normalized compositions of carbonates from electron-probe microanalysis in mol% oxides. Dominant cements are Mn-calcite. Note substitution of MgO is minor.

Figure 5. Depth plots for Site C0011 of $\delta^{18}\text{O}$ (A) and $\delta^{13}\text{C}$ (B) of carbonates, temperatures from carbonate clumped isotope measurements (C), and measured $\delta^{18}\text{O}$ of interstitial water and calculated $\delta^{18}\text{O}$ of fluids in equilibrium with carbonates from carbonate clumped isotope analysis (D). Roman numerals show intervals of lithologic units I through V for Site C0011; SMTZ is depth of sulfate-methane transition zone (Expedition 333 Scientists, 2012b). Carbonates are keyed to mineralogy by symbol. Circled symbols in A and B denote samples analyzed for clumped isotopes. Dashed fields highlight carbonates with isotopic signatures dominated by deeper characteristics. Small gray circles in B are $\delta^{13}\text{C}$ values of dissolved inorganic carbon (DIC). Gray fields show expected ranges of isotope signatures for cements precipitated in equilibrium with seawater-like fluids. Note the preservation of seawater-like $\delta^{18}\text{O}$ values in some of the deeper samples. C. Temperatures of carbonate formation determined with the clumped isotope method follow the geotherm of Marcaillou et al. (2012). The geotherm is based on borehole measurements in the upper 180 mbsf and is extrapolated to depth using core-based measurements of thermal conductivity of the sediments (Expedition 333 Scientists, 2012b). The clumped carbonate temperatures generally lie close to the geotherm, with the exception of 3 samples (see text for discussion). One standard error in temperatures are shown by horizontal lines where larger than symbol. D. $\delta^{18}\text{O}$ of waters during carbonate formation determined from clumped isotope temperatures and fractionation expression of Kim and O'Neil (1997) for calcite. Gray circle shows an example of one possible correction of the oxygen isotope value for a sample that is ~90 wt% rhodochrosite-siderite (see text for discussion). Gray ovals are $\delta^{18}\text{O}$ values of interstitial waters squeezed from core samples. The clumped water isotopes are generally higher than modern IW. Carbonate isotope values are relative to Vienna PeeDee Belemnite standard (V-PDB); water values are relative to Vienna Standard Mean Ocean Water (V-SMOW).

Figure 6. Stable isotope data from Site C0012, with same plots and symbols as in Figure 5. A and B. Lowest three samples are two pelagic mudstones just above basalt, and a calcite vein in basalt. Circled symbols were analyzed for clumped isotopes. $\delta^{13}\text{C}$ values of carbonates are more depleted in ^{13}C than expected for equilibrium with DIC, the trends generally are parallel in Lithologic Units IV and V. C. As with C0011, C0012 clumped temperatures define a trend that is subparallel to the geothermal gradient; only four samples

have temperatures within one standard error of the gradient. The deep, low-temperature sample is ~45% dolomite consistent with formation early at shallow depths, and then subsequent burial (see text for discussion). The shallowest sample and three of the four deepest sediment cement samples have temperatures in excess of the modern gradient and likely did not precipitate in equilibrium with current temperatures, suggesting slightly warmer conditions prevailed at a time in the past. D. $\delta^{18}\text{O}$ of waters during carbonate formation determined from clumped isotope temperatures at Site C0012 are further from equilibrium for several samples than at C0011. Roman numerals show intervals of Lithologic Units I through VI for Site C0012 (Expedition 333 Scientists, 2012ab).

Figure 7. Strontium isotope ratios and barium concentrations of pore fluids (black squares) and carbonates (triangles) from IODP Sites C0011 (A) and C0012 (B). Manganese concentrations are shown for C0011 and C0012 only. Circled symbols in Sr plots are samples with clumped isotope measurements. Data for IODP Site U1329 (C) (Cascadia margin, Joseph et al., 2013a) are included for comparison (see discussion). Strontium isotopic composition of oceanic crust (Staudigel et al., 1981), ash (Joseph et al., 2013a) and contemporaneous seawater values (Hess et al., 1986; Veizer et al., 1999) are illustrated for comparison. Sr isotope data from Joseph et al. (2013ab). In carbonates, barium/calcium ratios ($\mu\text{mol/mol}$) are measured by ICP-OES, manganese/calcium ratios ($\text{wt}\% \times 10/\text{wt}\%$) by microprobe.

Figure 8. Plot of carbonate formation temperature compared with $\delta^{18}\text{O}$ values of fluids calculated using fractionation expression of Kim and O'Neil (1997). Δ_{47} values corresponding to temperatures are based on the calibration from Tripati et al. (2015). Dashed lines and per mil values relative to SMOW of corresponding carbonates are shown with dashed lines. Moving from left to right represents increasing burial and temperatures. Carbonates formed under conditions of increasing burial in open marine conditions would plot as a field centered on $\delta^{18}\text{O}$ equal to $\sim 0\text{‰}$. Carbonate oxygen isotope values are pulled to higher numbers if heavier waters are released from diagenesis of smectite to illite, represented by "clay-bound water". Negative $\delta^{18}\text{O}$ values result if heavier oxygen is fractionated into newly formed clays during alteration of volcanic matter or other reactive silicate minerals. Most carbonates likely formed from waters dominated by marine isotopes with an important component of lighter waters from silicate alteration. A few samples with positive $\delta^{18}\text{O}$ values indicate ingress of clay-bound waters from clay mineral diagenesis. Note there are two samples corrected to lower $\delta^{18}\text{O}$ values (gray data symbols) because they either are dominated by dolomite ("D"; Sample 333-12D-6H-1, 13-14) or rhodochrosite-siderite (RS; 322-11B-45R-4, 86-88).

1259

1260 Figure 9. Model of carbonate formation with depth. Upper zone (A) of cementation (gray
1261 layers) contains calcite, Mn-calcite, R-S, and dolomite, indicating reduced manganese and
1262 iron in pore waters. Carbonate is low in barium because of barite precipitation above the
1263 sulfate-methane transition zone. $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$ values are high due to seawater-
1264 dominated pore waters and low temperatures, respectively. Dissolved inorganic carbon was
1265 likely ^{13}C depleted in sulfate-methane transition zone. With increasing burial (B) carbonates
1266 dissolve and locally re-precipitate. At greater depth (C) progressive ash alteration has
1267 lowered $^{87}\text{Sr}/^{86}\text{Sr}$ values in pore waters resulting in somewhat lower strontium isotope ratios
1268 in carbonate. Variations in manganese and higher barium in carbonate reflect pore water
1269 compositions. $\delta^{18}\text{O}$ and carbonate clumped temperatures are consistent with recrystallization
1270 of carbonate cements to approach equilibrium with *in situ* pore waters.

Table 1. Carbonate chemistry

TABLE 1. CARBONATE GEOCHEMICAL DATA					
sample number	depth (mbsf)	$\delta^{18}\text{O}$ (‰)†	$\delta^{13}\text{C}$ (‰)	$^{87}\text{Sr}/^{86}\text{Sr}$	Ba/Ca (mmol/mol)
<u>C0011B-</u>					
8R7, 34-36	422.19	-1.89	-3.91	0.708086	13.8
8R7, 66-68	422.41	-7.03	-20.14	0.708507	0.6
12R3, 102-104	444.02			0.708351	5.5
13R5, 73.5-77.5	455.82	-3.43	-2.58	0.707774	3.3
14R1, 47-49	460.47	-0.17	-18.47	0.708468	0.3
32R1, 107.5-109	597.00	-6.78	-13.59		
32R1, 122-123.5	597.15	-0.95	-21.56	0.708692	1.7
33R3, 57-58	607.05	-4.74	-23.36	0.708560	0.8
33R4, 50-51	608.75	-3.40	-7.05	0.707785	4.7
33R5, 65-67	610.40	1.65	-12.58	0.708534	3.7
38R6, 17-19	659.34	-0.43	-10.54	0.708126	5.4
39R2, 39-41	664.22	-6.40	-15.21	0.708503	0.6
41RCC, 5-7	678.60	-6.06	-20.67	0.708480	0.8
45R1, 54-56	699.04	-1.83	-6.93		
45R4, 86-88	701.67	-1.87	-10.07	0.708237	2.2
48R2, 21-22	722.21	-0.30	-7.45	0.708179	4.8
50R2, 45-46	739.25	-3.36	-7.02		
50R3, 31-32	740.61	-2.22	-5.93	0.708463	1.2
51R1, 107-108	748.47	-11.88	-11.25		
51R3, 29-31	750.54	-10.34	-11.49	0.707910	0.1
51R6, 92-94	754.43	-0.97	-6.84	0.708408	3.4
51R7, 15.5-16	753.74	1.27	-10.21	0.708555	1.3
52R5, 33-35	762.56	-9.94	-8.78	0.708456	0.4
57R3, 73-75	849.67	-10.46	-14.43		
59R1, 111-113	865.64	-11.86	-19.66		
<u>C0011D-</u>					
11H8, 95-96	108.31	-0.73	-0.25		
13H7, 11-12	125.34	-0.60	0.34		
26X2, 58-59	206.43	-1.10	-2.55		
27X5, 127-128	214.48	-1.48	-0.16		
29X2, 112-113	222.32	-2.60	0.26		
30X3, 125-127	228.88	-1.31	-0.93		
31X1, 69-70	242.19	-1.08	-2.03		
31X5, 97-98	239.42	-1.60	-0.93		
33X4, 64-65	249.81	-0.66	-1.11		
34X1, 65-66	252.15	-2.72	-0.52		
36X3, 64-65	269.47	0.50	-3.42		
37X2, 11-12	276.99	-1.82	-3.21		
38X6, 72-73	288.40	-1.43	-2.07		
39X3, 96-97	295.77	-1.44	-2.48		
40X7, 83-84	309.20	-1.38	-2.15		
41X7, 82-83	319.01	-0.58	-1.41		
<u>C0012A-</u>					
12R2, 43-44	150.86	3.98	-13.18		
16R1, 5-7	188.95	-3.53	-17.23	0.708182	0.6
20R1, 73-74	225.23	3.10	-13.34	0.708553	0.8
20R4, 118-119	230.18	3.72	-12.18	0.708293	1.5
31R4, 103-105	332.10	-4.75	-15.60	0.708391	1.0
32R1, 73-76	339.40	-7.44	-19.51	0.708135	0.2
34R1, 129-131	358.29	-9.40	-15.65	0.707922	0.5
36R3, 48-50	378.15	-8.61	-17.45	0.708337	0.3
39R4, 6-8	408.44	-2.56	-13.22	0.707991	1.5
40R6, 11-22	419.86	-11.40	-16.74		
41RCC, 12-13	429.75	-12.23	-18.72	0.707264	0.1
46RCC, 36-40	474.44	-11.34	-22.48	0.707149	1.7
47R2, 30-35	481.07	-3.56	-0.65		
<u>C0012C-</u>					
7H4, 124-125	55.85	-1.91	-0.32		

<i>8H8, 47-48</i>	69.17	-0.97	-0.10
11H5, 24-25	91.42	-0.22	-2.01
12H3, 76-77	97.59	-3.39	-2.44
15H7, 46-47	123.49	-0.50	-0.96
<u>C0012D-</u>			
<i>2H8, 30-31</i>	125.18	-1.38	-0.47
4H1, 84-85	134.84	-2.02	-2.23
4H5, 81-82	139.07	-6.84	-10.61
<i>6H1, 13-14</i>	146.63	5.70	-11.19
6H3, 8-9	149.41	0.53	-7.20
6H5, 14-15	149.96	1.23	-8.67
11H5, 16-17	172.80	-2.83	-6.70
11H5, 58-59	173.22	-3.46	-6.29
11H5, 95-96	173.59	-3.15	-4.18
11H5, 110-111	173.75	-1.24	-4.75
13H5, 48-49	180.50	-1.60	-1.78
13H5, 71-72	180.90	-3.20	-17.03
<u>C0012E-</u>			
3X8, 57-58	526.67	-15.96	-8.78
<u>C0012G-</u>			
1R1, 44-45	515.44	-4.23	-0.10
1R1, 51-52	515.51	-2.20	0.09

Note: Holes C0011B and C0012A drilled during IODP Expedition 322; Holes C0011D, C0012D, C0012E, and C0012G drilled during IODP Expedition 333.

Sample numbers in italics have carbonate clumped isotope data presented in Table 2.

*Permil values vs. Vienna PeeDee Belemnite standard.

†⁸⁷Sr/⁸⁶Sr data normalized to National Bureau of Standards standard NBS 987, with a reported ⁸⁷Sr/⁸⁶Sr value of 0.710245. A mean value of 0.710225 ± 0.000052 (2σ mean; n = 91) was obtained for repeated measurements. Strontium concentrations in carbonates were not determined.

§N.D. = not determined.

Table 2. Clumped data table

TABLE 2. CARBONATE CLUMPED ISOTOPE DATA												
Sample number	n =	□□□□□ (mbsf)	$\delta^{13}\text{C}$ mineral (‰) ¹	$\delta^{13}\text{C}$ 1 s.e.	$\delta^{18}\text{O}$ mineral (‰)	$\delta^{18}\text{O}$ 1 s.e.	Δ_{47}^* (‰)	Δ_{47} 1 s.e.	$\Delta_{47} T$ (°C) ²	T (°C) 1 s.e.	Water $\delta^{18}\text{O}$ (‰) ³	Water $\delta^{18}\text{O}$ 1. s.e. ⁴
C0011B-												
8R7, 66-68	3	422.41	-20.127	0.008	-6.439	0.013	0.650	0.003	35	1.0	-2.1	0.2
33R3, 57-58	8	607.05	-23.466	0.038	-3.913	0.016	0.633	0.009	40	2.8	1.4	0.5
39R2 39-41	2	664.22	-14.541	0.015	-6.323	0.160	0.645	0.011	37	3.2	-1.7	0.8
45R4,86-88	1	701.67	-10.191	0.004	-2.207	0.014	0.631	0.010	41	3.2	3.2	0.6
51R1, 107-108	2	748.47	-10.668	0.004	-11.517	0.057	0.583	0.015	57	5.5	-3.4	1.0
51R3, 29-31	2	750.54	-10.836	0.071	-9.993	0.178	0.565	0.028	63	10.5	-0.8	1.9
52R5 33-35	2	762.56	-8.614	0.042	-10.330	0.094	0.571	0.012	61	4.4	-1.5	0.8
C0011D-												
13H7, 11-12	2	125.34	0.318	0.035	-0.154	0.006	0.720	0.037	17	9.0	0.5	1.9
33x4, 64-65	5	249.81	-1.578	0.624	0.083	0.156	0.722	0.009	16	2.2	0.7	0.6
36x3, 64-65	3	269.47	-2.667	0.854	-0.630	0.695	0.699	0.022	22	5.5	1.1	1.8
C0012A-												
16R1, 5-7	5	188.95	-16.579	0.014	-3.169	0.122	0.670	0.015	30	4.1	0.1	0.9
32R1, 73-76	1	339.40	-18.922	0.007	-8.011	0.012	0.616	0.010	45	3.3	-1.8	0.6
34R1, 129-131	2	358.29	-16.028	0.046	-7.220	0.068	0.611	0.007	47	2.3	-0.7	0.5
40R6, 11-12	1	419.86	-16.098	0.006	-11.589	0.005	0.568	0.009	62	3.2	-2.6	0.5
41RCC, 12-13	2	429.75	-19.631	0.157	-11.845	0.777	0.576	0.007	59	2.5	-3.3	1.2
46RCC, 36-40	1	474.44	-22.390	0.007	-10.077	0.011	0.551	0.012	68	4.6	-0.1	0.7
47R2, 30-35	1	481.07	-1.179	0.009	-2.540	0.025	0.754	0.035	8.7	7.7	-3.6	1.8
C0012C-												
8H8, 47-48	2	69.16	0.003	0.117	-0.011	0.060	0.707	0.017	20	4.3	1.3	1.0
C0012D-												
6H1, 13-14	2	146.63	-11.354	0.036	4.332	0.197	0.722	0.024	16	5.8	4.9	1.4
C0012E-												
3X8, 56-57	4	526.67	-9.158	0.279	-12.941	0.296	0.589	0.009	54	3.2	-5.2	0.8

. Average of temperatures are shown in figure 4.

*absolute reference frame (ARF) corrected value

1 Mineral $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ relative to Vienna PeeDee Belemnite standard.

2 Temperature and calculated water $\delta^{18}\text{O}$ values are means of replicates using calibration of Tripathi et al. (2015)

3 All $\delta^{18}\text{O}$ of water relative to Vienna Mean Standard Ocean Water standard. Values calculated from clumped-isotope temperatures using fractionation expression for calcite (Kim and O'Neil, 1997) without correction for other carbonate phases.

4 Calculated based on standard error of temperatures and carbonate $\delta^{18}\text{O}$ values.

Figure 1. Location map

Sample et al. Figure 1

Figure 2. Stratigraphy

Sample et al. Figure 2

Figure 3. Textures

Sample et al. Figure 3

Sample et al. Figure 4

Figure 5. C0011 isotopes

Sample et al. Figure 5

Figure 6. C0012 isotopes

Figure 7. Sr and Ba

Sample et al. Figure 7

Figure 8. Rock-water interaction

Sample et al. Figure 8

Figure 9. Summary figure

Sample et al Figure 9