The thermal imprint of continental breakup during the formation of the South China Sea

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The stretching of continental lithosphere results in asthenospheric upwelling, raising of isotherms, melting during decompression and eventually seafloor spreading. The thermal maturity of overlying sedimentary organic matter from these settings would be expected to be distinctly altered by these processes, however this is still poorly constrained and quantitatively unexplored. International Ocean Discovery Program (IODP) Expeditions 367–368 cored sediments at the Continent Ocean Transition (COT) on the Northern Margin of the South China Sea (SCS). From two settings at the South East China COT we measured and modelled thermal maturity in pre-/syn- to post-rift sediments making use of a range of thermal maturity parameters. Various heat-flow evolutionary scenarios were investigated, with notable jumps in thermal maturity for sediments corresponding to different depositional packages. In order to match observations of thermal maturity, it was found that the deeper and likely pre-rift sediments were heated to temperatures as high as 200 °C during initial breakup. Achieving this temperature for the deeper sediments requires that significant additional heat be imparted at shallow depths (e.g. exposure to at least the far-field effects of a magmatic intrusion or subsurface expressions of volcanism). The post-rift sediments have lower thermal maturities which are likely due to limited burial and the absence of late post-rift magmatism. The comparison of the SE China COT with other margin examples highlights some parameters controlling the thermal evolution and its record.

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1. Introduction

The thermal structure of rifted margins depends on the amount of thinning of the continental lithosphere, the time elapsed since breakup (i.e. cooling duration), the amount of radiogenic-heating supplied by the residual continental crust and lithospheric mantle (McKenzie, 1978; Slater et al., 1980). During continental extension isotherms initially rise, but this period of heating is followed by progressive cooling as the rifted continent transfers heat by conduction to overlying sediment (Royer et al., 1980). Modelling this evolution with accurate stratigraphic and petrophysical properties, e.g. thermal conductivity, allows prediction of the thermal evolution of extensional systems. When applied within a basin model where calibration is used, modelling processes such as hydrocarbon generation allows dynamic parameters such as pore pressure to be predicted (Peters and Nelson, 2012). However, at many Continent Ocean Transitions (COT), current heat-flow measurements differ greatly from predictions (Lucaseau et al., 2008; Nissen et al., 1995) highlighting the lack of calibration for thermal modelling in such settings. Deep boreholes, seismic images, geophysical data and field studies at COT reveal complex deformation modes and associated magmatism and hydrothermal fluid circulation (Jagoutz et al., 2007; Larsen et al., 2014; Manatschal, 2004), all of which impact to different extents thermal evolution and heat transfer mechanisms during and after rifting.

Previous studies have investigated the thermal maturity of organic matter dispersed in sediments at COT using deep borehole data (Peace et al., 2017; Pross et al., 2007), or sedimentary successions preserved along fossil margins stacked in mountain belts that escaped pervasive syn-organic metamorphic overprint (Clerc and Lagabrielle, 2014; Lescouët et al., 2019). However, at COTs basin models are often unreliable due to the lack of distal deep boreholes, the lack of samples to provide measurements to cal-
ibrate models and the difficulty of incorporating fluid flow and igneous events in basin models (Gardiner et al., 2019). Here we report new thermal maturity data from two holes located at the SE China COT, where petrophysical data, heat-flow measurements and thermal maturity observations better constrain the thermal evolution. The intent is that future work can compare the COT rifted margin to others in order to construct better thermal models for COT.

Sites U1499 and U1502 were drilled during IODP Expeditions 367–368 on the SE China COT. Holes at these sites penetrate sedimentary, magmatic and hydrothermally altered sediments and rocks located at the most distal SE China continental margin (a location with extreme lithospheric thinning and crustal thickness <10 km). This unique dataset permits the investigation and modelling of the in situ thermal history of pre- syn- and post-rift sediments and from this can be deduced the thermal effects of the rifting processes that formed the South China Sea.

2. Geological setting and structure of the SE China distal margin

The SE China margin is located along the northern edge of the SCS oceanic basin (Fig. 1) that propagated from NE to SW between ~33 Ma and ~15 Ma (Brias et al., 1993; Taylor and Hayes, 1983). Previous studies (e.g. Franke et al., 2014) complemented by IODP Expedition results (Larsen et al., 2018b) reported a major Eocene rifting phase followed by early Oligocene breakup (~30 Ma) on the SE China distal margin. The investigated segment of the distal SE China margin is ~90 km long (Fig. 1B, Fig. 2) and presents a progressive thinning of the continental crust which eventually tapers off passing abruptly in space and time to igneous ocean crust (Larsen et al., 2018a) (at ~85 km on Fig. 2b). IODP expeditions 367–368 and 368X penetrated the acoustic basement at 6 locations. The top of the acoustic basement is recognized as the Tg-reflector (Fig. 1B–2) and corresponds to the base of the Cenozoic succession (Zhou et al., 1995). Along this segment, distinct tectonic structures were recognized from the continent to the ocean; namely the Outer Margin High (OMH), and the ridges A, B and C.

The OMH (to the northwest in the profile of Fig. 2) is formed by a 15 to 20 km thick continental crust that includes pre-rift sediments and metamorphic rocks sampled below the Tg reflector at Sites U1501 and U1504, respectively. The COT presents a progressive thinning of the continental crust characterized by a gradual rise of the Moho up to the 7–8 km thick ridge A (Fig. 2). This ridge was sampled at two sites (U1499 and U1502). Highly altered Mid-Ocean Ridge Basalts (MORB) are recovered at Site U1502 (Fig. 2), whereas 40 km to the west, at Site U1499 pre- to syn-rift clastic sediments are present confirming the continental nature of ridge A (Fig. 2) (Larsen et al., 2018a; Nirren et al., 2020).

Ridges B and C are 7 km thick and represent landward rotated fault blocks penetrated respectively by sites U1500 and U1503. At both of these sites MORB with pillow structures are present and here a magnetic anomaly C11n dates the crust to 30.0 Ma (Larsen et al., 2018a and Fig. 2) and constrains the breakup age to early Oligocene. Seismic observations, gravity modelling and the analysis of crustal bulk densities further confirm the location of the continent ocean boundary between ridges A and B (Nirren et al., 2020). As a result, ridge A represents the last remnant of continental crust in the investigated segment, recording extreme lithospheric thinning and the onset of MORB magmatism during final rifting.

3. Structure and sedimentary sequence of ridge A

Ridge A can be mapped across the margin’s entire segment (Fig. 1) (~90 km). This basement high has significant morphological variations, characterized by a narrow and sharp basement
geometry to the NE (Site U1502), passing to a rounded and blurred shape, 40 km to the SW (Site U1499) (Fig. 2). Based on seismic and borehole data, ridge A is interpreted as the last rotated continental fault block bounded by a major oceanward normal fault that juxtaposed the initial oceanic crust (Fig. 2).

Based on biostratigraphy and seismic architecture, the sedimentary succession of this area is divided into four units late post-rift (recent to the mid/early Miocene boundary 0–11.6 Ma), early post-rift (mid Miocene to breakup time in Oligocene 11.6–30 Ma), syn-rift (early Oligocene to Eocene) and pre-rift (undated, Fig. 2). Post-rift lithologies are similar at Sites U1499 and U1502, composed of alternating clay, silt and sand with variable amount of nannofossils. Located on this basement high, both sites show a very low early post-rift sedimentation rate of 8–10 mm kyr⁻¹ (Larsen et al., 2018b) that increases to 39–80 mm kyr⁻¹ during the late post-rift stage. This early to late post-rift sequences are delimited by the...
Fig. 3. Photographs and photomicrographs of the Sites U1502: a) Dolomitic marble alternating with meta-claystone located at less than 10 m from hydrothermally altered MORB (U1502B-3R-2); b) Cross polarized and analysed photomicrography of the fully recrystallised dolomitic marble (U1502B-3R-2); c) Highly altered basalt with relic of pillow structures (U1502B-27R-2); d) altered basalt crosstcut by branched epidote-calcite veins (U1502B-32R-2).

T32 reflector in seismic profiles. In contrast, the pre-Miocene (below T60 reflector) early post-rift and syn-rift stratigraphic record differs significantly between the two sites.

3.1. Early post-rift to syn- or pre-rift succession at Site U1499

At Site U1499, 927 meters below sea floor (mbsf) the early Miocene (early post-rift) reddish gray clay-rich chalk (Sun et al., 2018) passes to a 60 cm thick level containing iron-manganese nodules. Below, a 4 m thick matrix-supported breccia (Fig. 4) is dated from ~26 to ~30 Ma (Oligocene) representing the earliest post-rift sediments and the last age datum in the well (Sun et al., 2018). This breccia is composed of pebble size polymict angular sandstone clasts in a nanofossil rich claystone matrix (Fig. 4 (Sun et al., 2018)). This unit at Site U1499 is coeval to sediments intercalated within pillow basaltic lava of the first igneous oceanic crust sampled at U1500 (Larsen et al., 2018a) (Fig. 2). Below, cores penetrated the Tg reflector and are composed of 148 meters of undated gravels representing either syn- or pre-rift sequences. These gravels comprise polygenic cobble-sized clasts of former sandstones and siltstones but igneous clasts are not observed. Also present in this succession are poorly lithified clayey silt or silty sand intervals which while possessing laminae rich in organic matter, have low carbonate content and do not contain calcareous nanofossils (Sun et al., 2018). These sands and silts are interpreted as the matrix for the gravel (Fig. 4). It is likely that the matrix is under represented in core due to its washout during drilling operations. Clasts within the overlying earliest post-rift matrix supported breccia (Fig.4) are angular and comprise lithologies that are the same as the underlying gravel, indicating a possible reworking during the late syn-rift and earliest post-rift time interval.

3.2. Early post-rift to syn-rift succession at Site U1502

At Site U1502, the first 375 meters of Pleistocene and Pliocene sediment was not cored. At 739 mbsf, drilling penetrated early post-rift late Oligocene greenish gray biosiliceous claystone. The claystone is overlain by pre-late Oligocene light gray dolomitic marble or limestone that is intercalated with clays that have igneous clasts, meta-claystones and sandstone (Larsen et al., 2018c) (Fig. 3). Here the thin syn-rift sequence is about ~10 m thick (Fig. 3). The dolomitic marble is composed of ~95% recrystallized euhedral dolomite (Larsen et al., 2018c) (Fig. 3), which indicates a pervasive hydrothermal transformation of the initial protolith (Machel, 2004).

Underlying the syn-rift sediments, and beneath the Tg reflector at 749 mbsf is an igneous basement composed of basaltic breccias, brecciated-basalts with a jigsaw-like fit indicating hydraulic fracturing (Fig. 3). Hydrothermal fluid circulation is confirmed by the numerous veins with variable composition, from silica- and carbonate-rich to epidote-rich. The veins are interconnected networks and have branched geometries (Fig. 3). Despite hydrothermal alteration, pillow structures are still visible (Fig. 3) and the geochemical signature of the bulk rock is typical for a MORB (Larsen et al., 2018c).

Diagenesis of this sedimentary sequence records the thermal history of the distal rifted margin, in the following section we describe the sampling strategy of the cores and the analyses we conducted to determine the temperature history.

4. Approach and analytic methods

4.1. Sampling strategy

Sampling was guided by total organic carbon content (see Sun et al., 2018 and supplementary information), with preference given to organic matter rich intervals most likely to yield high quality data (e.g., those with a TOC > 0.5%, SI 1). The deepest units at the base of U1499 were sampled at a greater frequency because of their importance for capturing syn-rift thermal history), with both the matrix and the clasts of the pre- to syn-rift breccias sampled.

4.2. Vitrite reflectance

Vitrite reflectance Ro% is commonly used in the oil industry to evaluate the thermal maturity of organic matter dispersed in sediments (Suárez-Ruiz et al., 2012). This method is based on the microscopic observation of a single class of solid organic matter (huminite-vitrinite maceral group) whose molecular reorganization due to increasing temperature through time results in an increase of its reflectivity (Tissot and Espitalié, 1975). Samples for vitrinite reflectance were analyzed in reflected, non-polarized, monochromatic light (λ = 546 nm) under oil immersion (n = 1.518) using a Zeiss Axioskop MPM400 microscope equipped with MIPS 200 system by J&M Analytik AG. Standardization was performed using a Spinel with relative reflectance (R) of 0.426%; Saphir with R of 0.585%, YAG (Yttrium-Alluminium-Garnet) with R of 0.905% and GGG (Gadolinium-Gallium-Garnet) with R of 1.72.

Thermal maturity of each sample were defined according to the ASTM standard D7708-14. Here we take the immature stage of hydrocarbon generation to be indicated by Ro% values less than 0.5%,
the early stages of oil and hydrocarbon generation to correspond to Ro% values between 0.5 and 0.7% and the late stages of oil generation to occur between 0.8 and 1.35%. Vitrinite reflectance results are presented in Table 1 and their corresponding histograms in SI 2-3.

4.3. Raman spectroscopy

Raman spectra of carbonaceous matter provide a geothermometer across both metamorphic (T > 200°C) (Beyssac et al., 2002; Lahfid et al., 2010) and diagenetic temperature conditions.
(50–200 °C) (Lünsdorf and Lünsdorf, 2016; Schito et al., 2017; Schmidt Mumm and Inan, 2016; Wilkins et al., 2014), as well as within the thermal aureoles of magmatic intrusions (Muirhead et al., 2017). Micro-Raman spectroscopy was carried out using a Jobin Yvon LabRam system in a backscattering geometry. Data were collected in the first order Raman spectrum over the range 1000–2000 cm\(^{-1}\) using a 600 grooves mm\(^{-1}\) spectrometer grating and CCD detector and Neodinium-Yag green laser (532 nm) as a light source. Laser-induced degradation of kerogen and fluorescence-background signals were minimised by maintaining laser power below 0.4 mW. Using optical filters, the Raman backscattering was recorded with an integration time of 20 s for 6 repetitions. Each fragment was analysed with a 2 μm diameter spot using a 20× or a 50× optical power objective.

Raman analyses were only performed for Site U1499, and were performed on splits of the same samples used for vitrinite reflectance. During sample preparation analyses avoiding polishing with less than 0.1 μm slurry according to recommendation from Lünsdorf and Lünsdorf (2016). Measurements were taken on both vitrinite fragments and on the organic matter within the matrix (amorphous organic matter). We adopted two methods to deconvolve Raman spectra to obtain maximum paleo-temperature data. The first method is particularly suitable for low maturity samples and is based on a separate deconvolution of the D and G band regions (Fig. 4). After a linear baseline correction, the position, width and integrated areas of the D and G band are measured separately and converted into vitrinite reflectance equivalent (R\(_{eq}\)%) and maximum temperature is obtained following a multi-parametric equation according to (Schito and Corrado, 2018). Spectra indicating higher thermal maturity levels were analysed using an automatic approach, based on the D and G bands parameters, which directly returns the maximum paleo-temperatures acquired during burial (Lünsdorf and Lünsdorf, 2016) (Table 2).

4.4. Biomarker analysis

Samples for biomarker analysis were solvent extracted using Soxhlet apparatus (5–25 g of sediment or rock was extracted in dichloromethane/methanol 93:7 v/v for 48 h). The extract was fractionated using flash mini-column chromatography (silica column; hexane for saturated fraction; 3:1 v/v hexane/dichloromethane for aromatics fraction; 2:1 v/v dichloromethane/methanol for polar fraction). The resulting saturated fraction was analyzed by gas chromatography-mass spectrometry (GC-MS). GC-MS was performed using a 6890N Network GC system interfaced to a 5975 inert mass selective detector. A PTV in injector (300 °C) operating in split less mode was used and the GC temperature program was as follows; 60 °C to 120 °C at 20 °C min\(^{-1}\) then from 120 °C to 290 °C at 4 °C min\(^{-1}\). The column was Greyhound GC-5 (an HP-5 equivalent phase; 30 m length, 250 μm ID and 0.25 μm film thickness). The MS was operated in sim mode (less than 20 ions with a dwell time less than 40 ms). Compounds were identified by reference to well-characterized samples of bitumen of analogous thermal maturity. Inputs for biomarker thermal maturity parameters were obtained from peak areas measured on the \(m/z\) 191 ion chromatogram for hopanes and \(m/z\) 217 ion chromatogram for steranes (Fig. 5, Table 3 and SI 4).
5. Results

5.1. Site U1499

5.1.1. Late post-rift (0–840 mbsf)

Samples from the late post-rift sequence have a relatively low TOC (<1 wt%, Table 1 and SI 1) (Sun et al., 2018). The vitrinite data from 3 samples of the late post-rift sequence (Pleistocene to mid Miocene) show very low thermal-maturity values ranging between 0.26 and 0.41 Ro% (in the immature stage of hydrocarbon generation, Fig. 2, Table 1). Despite very high fluorescence that made analyses difficult, we were able to obtain six Raman spectra from sample U1499B-12R-1W (752 mbsf) that show very low maturity with an average value of Roeq% of 0.34 and a standard deviation of 0.13 (Table 2).

Biomarker thermal maturity indicators of thermal alteration include both the Hopane 22S (hereafter referred to as hop-22S) and sterane 20S parameter (see Table 3 and Fig. 5). As Raman and vitrinite reflectance they record a similarly low level of thermal alteration of organic matter in the late post-rift succession (Tables 1, 2, 3). The strongest assessment of a change in thermal maturity within this interval is obtained from the hop-22S parameter, which changes from 0.11 to 0.25 from 623 to 726 mbsf. This observation represents a slight increase in the parameter above its background level, but is important because the hop-22S parameter has a kinetic model (Mackenzie and McKenzie, 1983), which can be used to constrain thermal history in these sediments.

There are instances where thermal maturity parameters are high within the late post-rift sediment (Table 3), but most of these likely represent allochthonous organic matter as there is no indication of faulting or intrusive activity that might otherwise account for sudden downhole in situ changes in thermal maturity within the late post-rift succession. Additionally biomarkers such as sterenes or the proportion of ββ hopanes that are destroyed by exposure to hotter temperatures are still present (Amo et al., 2007; Farrimond et al., 1998), indicating that any high values must be explained by processes that do not involve heating of the host formation (e.g., thermal alteration of the biomarkers occurred prior to burial at the current location).

Thus, despite a high present-day heat flow (110 mW m−2), the late-post-rift sediments at site U1499 show a geologically mild thermal history, despite a high rate of burial in a rapidly subsiding basin.

5.1.2. Early post-rift (840–933 mbsf)

The early post-rift is composed of Miocene reddish claystone. In this interval, only biomarker data provided reliable results. Indications of a pre-oil window level of thermal maturity for the early Miocene red claystone are still present in the form of ββ hopanes and a hop-22S value of 0.38 (900 mbsf).

Below, in the earliest post-rift matrix supported breccia two samples at 932 and 933 mbsf show a thermal maturity at 0.59 and 0.66 Ro% respectively (in the initial portion of the oil window). Additionally, within this interval Raman spectra resolve clearly identifiable D and G bands indicative of organic matter that has experienced catagenesis (Fig. 4 D and G bands with a Roeq% of 0.65% std 0.18 calculated via Schito and Corrado, 2018), however there are Raman spectra indicative of a higher thermal maturity, indicating the presence of allochthonous organic matter (not included in the calculation of Roeq).

5.1.3. Gravel unit (syn- or pre-rift?) (933–1082 mbsf)

In the gravel unit, TOC values are highly variable between the different clasts and the matrix with the highest TOC content being 4.8 wt% (Sun et al., 2018). Vitrinite reflectance data in this oldest (pre-30 Ma) and deepest sampled unit are anomalously high when compared to the post-rift sequence. This gravel unit is characterized by an extremely rapid downhole increase in thermal maturity.
from 1.22 to 1.83 Ro% (from the upper part of the oil window to the gas window) across a 65 m thick section (respectively at 995 and 1062 m bsf) (Fig. 2). Thermal maturity of organic matter measured in the cobble-sized clasts is equivalent to that of the clay and silt matrix. This is an important observation because it indicates that both the large clasts that are most likely to preserve reworked organic matter, and the matrix that is likely to contain autochthonous organic matter have shared the same thermal evolution. Therefore, there is no evidence of a previous and more severe thermal history, inherited from the reworked sediment, recorded within the clasts.

It is also important to note that over a relatively short distance of 130 m, from the early post-rift Oligocene matrix-supported breccia Unit to the deepest sample of the syn- to pre-rift gravel Unit there is a large increase in thermal maturity (increase of 1.17 %Ro from U1499B-30R-6W, 932.98 mbsf to U1499-44R-1W 1062.64 mbsf in Table 1). In this unit the hop-225 parameter is above 0.55 and exceeds the oil window and would not therefore record further thermal alteration (Mackenzie and McKenzie,1983). Homogeneous Raman spectra (Fig. 4) were measured using the method presented by Lünsdorf et al., 2017. These samples showed maximum paleo-temperatures for a sandstone clast sample at 995 mbsf are 193 ± 38 °C (U1499B-37R-1W), and for a matrix sample at 1024 mbsf are 210 ± 35 °C (U1499B-40R-1W) (Figs. 4 and Table 2). The three different analytical techniques record a rapid increase in maximum paleo-temperatures and thermal maturity experienced by organic matter dispersed in the gravel unit.

5.2. Site 1502

5.2.1. Post rift

At site U1502, the post-rift section has TOC values lower than <0.7 wt% (Larsen et al., 2018c) and only three samples provided reliable vitrinite reflectance data. No reliable Raman analyses were obtained. The early and late post-rift sequences show a low thermal maturity with Ro% values from 0.29% to 0.38%. An anomalously high value of 0.57% Ro at 493.32 mbsf has been interpreted as re-worked dispersed organic matter. The upper part of the late rift succession at Site U1499, the hop-225 parameter is high (0.51 at 626 mbsf (Table 3) and indicates reworking of soluble organic matter during post-rift evolution

5.2.2. Syn rift

The syn-rift dolomitic marble has a vitrinite reflectance value of 0.43 Ro% at a depth of 739 mbsf indicating a pre-oil window thermal maturity, an observation consistent with a hop-225 value of 0.26 recorded at 744 mbsf that also indicates a pre-oil window thermal maturity. The close correspondence of these two independent measures of thermal maturity for the syn-rift succession at U1502 indicates that the data likely represent a true in situ thermal maturity. Although this overall level of thermal maturity for the syn-rift succession at U1502 is low with respect to hydrocarbon generation, for its relatively shallow depth (<800 mbsf) the syn-rift of U1502 is thermally mature (e.g. more thermally altered than an equivalent depth at U1499).

6. Modelling

To determine the thermal evolution of the SE China COT at ridge A, 1D basin models were produced using BasinMod 2D (Fig. 6). Basin models integrated porosity and thermal conductivity data measured for U1499 and U1502 (Larsen et al., 2018b). Different heat-flow scenarios were investigated. The first scenario used a constant heat-flow through time (Fig. 6). Temperature measurements acquired during piston coring at site U1499 give a present-day geothermal gradient of 93 °C/km and an estimated heat flow of 110 mW m−2 calculated using measured thermal conductivities of the sampled-sediments (Sun et al., 2018). The constant heat-flow model has a good correlation with the late post-rift section (above Tg) at both sites although it is unable to match the higher thermal maturity values in the earliest post-rift and in the gravel unit at Site U1499 (Fig. 6).

The second model is based on the depth independent lithosphere thinning model from McKenzie (1978), and referred to hereafter as the McKenzie type model. It assumes that heat flow increases due to the extension of continental lithosphere and fol-
allowed by a thermal post breakup re-equilibration (Fig. 7). We assumed a thinning factor of 4 (meaning a crustal thickness of 7.5 km for an initial crustal thickness of 30 km) which is in agreement with the observed crustal thinning at ridge A (Fig. 2). In this case, pre-rift heat-flow is set at 60 mWm$^{-2}$ corresponding to the average worldwide continental value (McKenzie, 1978). During the rifting phase of the SCS (40–30 Ma) the heat-flow increases up to 275 mWm$^{-2}$ and decreases exponentially to the current value of 110 mWm$^{-2}$ (Fig. 7c). This thermal evolution provides a thermal maturity curve very similar to the constant heat-flow model (Fig. 6), although, the obtained thermal maturity is slightly higher in the early post-rift sequence, compared to the previous model. These differences are small and cannot explain the high maturity values below Tg at Site U1499 (Fig. 6).

The third model includes the presence of an erosional event prior to the Cenozoic rifting with a constant heat-flow through time, using the present-day value (Fig. 6). In such scenario, the gravel unit of the Site U1499 is assumed to be pre-rift in age. A pre-rift erosional phase (pre-Tg) has been seismically reported and locally drilled in many localities across the SCS margins (Larsen et al., 2018a; Liang et al., 2019). The post-rift thermal maturity is alike the first model and the occurrence of 2.2 km of erosion before the Cenozoic rifting allows a fit to maturity values in the gravel unit, e.g. it predicts vitrine reflectance values of about 1.22 Ro% at 995 mbsf and 1014 mbsf (Fig. 4). Nevertheless, the modelled curve is not able to fit the deeper thermal maturity values around 1.7–1.8 Ro%.

Neither present day basal heat-flow, heating during prior episodes of burial nor heating due to lithospheric-thinning can supply sufficient heat to explain the gradient in thermal maturity measured in the gravel unit at the base of U1499. However, volcanism and related thermal effects have occurred at site U1502 in the form of hydrothermally altered MORB. It is thus geologically reasonable to investigate whether heating due to the presence of a magmatic body from which the MORB formed may explain the high thermal maturity in the pre-/syn-rift succession of U1499. To test if the high thermal maturity gradient recorded in the gravel unit can be recreated by heating within the aureole of a magmatic body we combined the results of the Basinmod 2D software with predictions made by the SILLi 1.0 software (Iyer et al., 2018). The SILLi software is designed to predict the effect of magmatic sills on the thermal maturity of a stratigraphic succession. In this case we assume that beneath the pre-/syn-rift gravel unit or nearby is a magmatic body. The intrusion was assumed to have been emplaced during the early Oligocene, during breakup. A set of models was performed to test the depth and size of the intrusion that could best recreate measured thermal matures. The best fit was obtained by a body 200 m thick located at 1150 mbsf (or 70 m beneath the TD of hole U1499B). Sensitivity tests are provided in Supplement (SI-6). It is worth noting that this solution is not unique and different sizes, depths and numbers of intrusion could also fit measured data.

7. Discussion

7.1. Tectonic and thermal evolution of the SE China COT

We analysed the thermal maturity of the sedimentary record on the most distal thinned continental crust of the SE China rifted margin to assess the thermal effect of rifting and breakup processes. The tectonic and thermal evolution observed at ridge A are summarised in Fig. 7.

An extreme thinning of the Eocene continental lithosphere is recorded at Ridge A. This thinned crust is directly juxtaposed to the MORB-type volcanic rocks found at Ridges B and C, which correspond to the onset of seafloor spreading at 30 Ma (Larsen et al., 2018a). The gravel unit at Site U1499 is either an initial coarse syn-rift sedimentary infill or older pre-rift sediment. Due to limited burial (less than 500 m), thermal effects of crustal thinning are not well recorded in the sediment-fill deposited at the earliest stages of rifting, despite the expectation that heat-flow would have increased during lithospheric-thinning (McKenzie, 1978) (Fig. 7).
During the latest stages of rifting, MORB type volcanism may have had a surface expression as is the case for the basaltics found at U1502, but it should also be noted that such magmatism can also thermally alter older sediment-fill as is seen in the pre-/syn-rift sediments at U1499. Mechanistically this would be done by magma intruding into sediments during late syn-rift stages; an intrusion would rapidly increase temperature for a geologically short duration, by locally increasing heat flow and thermally altering sediment within contact aureoles (Fig. 7: Fjeldskaar et al., 2008; Muirhead et al., 2017; Peace et al., 2017).

At Site U1502, volcanic rocks and a short 10 m interval of the overlying sediments are hydrothermally altered, but alteration is absent in the overlying 720 m of post-rift sequence. It is important to note that the deepest thermal maturity measurement at site U1502 is indeed higher than might be expected for its depth (with less than 750 m of burial thermal maturity at U1502 equals that found at 2 km in other sedimentary basins e.g. Farrimond et al., 1998). But despite the evidence of an active hydrothermal system, the thermal alteration evidenced in both vitrinite reflectance and biomarker data was explained by burial metamorphism with a heat flow of 275–110 mW m⁻² (Fig. 6). Thus it seems that hydrothermal fluids have probably not affected the organic matter at U1502, at least not directly. Hydrothermal fluids can certainly alter thermal maturity at both spreading centres (Simonetti et al., 1984), and in back arc basins (Bowden et al., 2016). But it is commonly acknowledged that short lived fluid pulses may not alter sedimentary organic matter if not sustained for sufficient duration (Parnell, 2010). Thus an interpretation of the presence of hydrothermal mineral phases indicating temperatures greater than 200 °C (Larsen et al., 2018c), but without alteration of sedimentary organic matter, would be that hydrothermal activity is less efficient at transferring additional heat to sediments than magmatism in the SE China COT. This may reflect the hydrothermal system at U1502 operating for only a short time, or the hydrothermal system waning significantly by the time overlying sediment was deposited.

In the earliest post-rift gravels of Site U1499 (~5 m of matrix supported breccia), thermal maturity is less than the deepest gravel unit (0.59–0.66 Ro% cf. 1.6–1.8 Ro%), and is only slightly more than would be predicted by a constant heat-flow model (Fig. 6). We offer two explanations for this observation. First, magmatic activity and associated thermal effects may have continued for a few million years after breakup, and subsequently waning magmatic activity changed thermal maturity (Fig. 7). A second explanation is that a true in-situ thermal maturity was not measured, and that our vitrinite and Raman data are strongly biased towards organic matter reworked from the underlying gravel unit. The effect of magmatism on the thermal maturity of the SE China COT is clear, however, the emplacement of this breakup related magmatism was likely spatially heterogeneously distributed across the
COT causing important variations within the thermal maturity of the pre- and syn-rift and potentially earliest post-rift sediments.

Soon after the phases of extensional break-up and localisation of magmatism at spreading ridges the SE China COT passively subsided. The post-rift succession has a low thermal maturity and is in the immature stages of hydrocarbon generation at sites U1499 and U1502. The thermal maturities of the post-rift successions at these two sites can be explained by basal heat flows that are constant over time or match a McKenzie-type thermal evolution (Fig. 6). The lack of differentiation between the two models of heat flow maybe due to limited burial and a low early post-rift sedimentation rate (∼8–10 mm yr⁻¹). From 30 to 11 Ma, less than 100 m thickness of early post-rift sediments was deposited. This lack of burial prevents significant differences in thermal maturity developing between the McKenzie type and constant heat-flow models, as they differ mostly during rifting and early post-rift times. The late post-rift sequence is thicker, but after 20 Ma the heat-flow had already reduced significantly compared to the breakup phases (Fig. 7).

7.2. Factors controlling thermal evolution and maturity of sediments at COT

Late syn-rift magmatism plays a prominent role in the thermal evolution of the SE-China COT. However, parameters controlling the thermal evolution and thermal maturity of sedimentary succession at COT are multiple and present complex interplays in time and space as exemplified in previous works and summarized in Fig. 8. In this section, we aim to provide an overview of the main factors favouring a regime of high heat-flows and temperatures in distal rifted margins and how they are recorded in sedimentary successions.

The thinning of the continental lithosphere, and the associated rise of the asthenosphere that compresses the isotherms and subsequently increases the geothermal gradient, is a major factor in regional thermal evolution (McKenzie, 1978) (Fig. 7). Different modes of lithospheric thinning (e.g. simple-shear, pure-shear, depth dependent thinning) variably affect heat-flows and their spatial distribution as well as their evolution during and after extension (Buck et al., 1988; Driscoll and Karner, 1998; Kusznirov and Karner, 2007). In the case of the SCS, heat-flow measurements suggest a pure-shear mode of extension (Nissen et al., 1995). However, in the segment of the SE-China margin that we investigated, the effect of late syn-rift magmatism and the limited number of wells precludes any unambiguous determination of the thinning mode based on thermal data.

Radiogenic heat production from residual continental crust represents another parameter with the potential to influence thermal evolution at rifted margins. This parameter is variable depending on the pre-rift history and the composition of continental crustal rocks (Jaupart and Mareschal, 2015). Radiogenic heating has been shown to be caused by Mesozoic granitic batholiths that are present across the SCS (Savva et al., 2014), and may locally contribute to heat-flow, and may be partly responsible for high heat-flows in the region (110 mW m⁻²).

Rifting and eventually breakup may induce additional heating through various heat-transfer mechanisms, all of which could locally increase thermal maturity. In this case, a modelled syn-rift magmatic intrusion increases the thermal maturity of the lowermost sedimentary succession at Site U1499 sufficiently to explain observed thermal maturation. The effect of an isolated magmatic intrusion is limited and only affects the surrounding sediments of approximately 1.5–2 times the width of the intrusion (Fjeldskaar et al., 2008). However if several magmatic sills are emplaced across a sedimentary succession, which is probable, this additional heat may significantly influence thermal maturity across a sedimentary basin as seen in the Rockall Trough (Fjeldskaar et al., 2008; Muirhead et al., 2017). Magmatism is often related to hydrothermal fluids, which play an important role in the COT by enabling the transfer of elements and heat between the mantle and superficial sediments (Pinto et al., 2015). However, as exemplified at Site U1502, hydrothermal activity needs to be sustained over time in order for organic matter to be significantly altered (Parnell, 2010). In the case of mantle exhumation in the COT of regions such as the West Iberian or the fossil Alpine margins, the serpentinization process may contribute to elevating or maintaining high-flow conditions during late-syn-rift or early post-rift stages (Callies et al., 2018).

Syn- and early post-rift sedimentation rates and therefore burial are crucial to recording the high heat flow conditions during early post-rift phases. In contrast to the SE-China COT, the Pyrenean fossil hyper-extended rift basin is characterized by pre-rift evaporites, massive syn-rift and early post-rift sedimentation, that blanket and bury sediment leading to the recording of high thermal maturities in organic matter (Clerc and Lagabrielle, 2014). Without significant burial (∼3–6 km in the Pyrenean case study (Clerc and Lagabrielle, 2014)), the temperature at the base of a sedimentary succession would never be great enough even were a geothermal gradient high (>80 °C km⁻¹).

Late post-rift magmatism is not indicated by our dataset while it is inferred in other localities of the SE China margin and clearly mapped in the oceanic domain of the SCS as shown by occurrence of several seamounts (Sibuet et al., 2016). Post-rift volcanism at a COT modifies the thermal regime in a way similar to that seen in the high local heat-flows in places such as the Gulf of Aden (Lucazeau et al., 2009). Such post-rift anomalous high heat flows alter the thermal maturity acquired during burial and cooling of the rifted margin. Elevated post-rift heat-flows have also been related to small-scale convection cells, formed by the difference in temperature difference between continental and oceanic lithosphere (Lucazeau et al., 2008). The operation of such convection cells for either a limited time-period or a very long time-period is not well constrained but may have a major impact on the COT thermal
evolution and therefore on the thermal maturity of associated sedimentary basins.

8. Conclusion

Despite progress in our understanding of the formation of rifted margins, the thermal evolution of COT remains a matter of debate. IODP expeditions 367–368 provided an opportunity to sample and model the thermal evolution on the thinnest continental crust of the SE China margin represented by Ridge A. The last fragment of the residual continental crust drilled by these expeditions is directly juxtaposed against the oldest oceanic crust and has been sampled by two drilling sites U1499 and U1502. Based on vitrinite reflectance, Raman spectroscopy and biomarker analysis, rapid changes in thermal maturity with depth are observed at Site U1499 in the oldest rift sediments. Present day heat-flows and heat-flow modelled according to a McKenzie-type rifting environment could not explain measurements of thermal maturity in the deepest sediments encountered. The heat-flow needed to recreate the high thermal maturity in the deepest section can only realistically be explained by syn-rift magmatism, notably encountered at the adjacent Site U1502. While of high thermal maturity for its shallow depth of burial, the early post-rift succession of U1499 and U1502 is notably less thermally mature.

Ultimately, the thermal evolution of COTs results from the interactions of several different parameters that challenge the current understanding of such domains. Beside the regional effect of lithospheric thinning, local thermal perturbations generated by magmatic additions during and after extension, as well as poorly constrained deep thermal anomalies during post-rift phases, may significantly affect the local thermal evolution of a COT.

Author contributions

M.N., G.M. and S.B. sailed on IODP Expedition 367/368 and are responsible for the sampling of the cores. M.N. and G.M. had the idea to test the thermal imprint of breakup on the SE China COT. A.S. S.C. and L.G.G. perform the vitrinite measurement and the Raman spectroscopy at Roma Tree University. S.B. analysed and modelled biomarkers. A.S. and M.N. adjusted the 1D thermal models. M.N., G.M., A.S., L.G.G., S.B. and F.D. have analysed the data and modelling results and all contributed to the redaction of this manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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Appendix A. Supplementary material

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